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## COEFFICIENTS OF SLIP IN GASES AND THE LAW OF REFLECTION OF MOLECULES FROM THE SURFACES OF SOLIDS AND LIQUIDS.

By R. A. Millikan.

Abstract.

**First order correction term to Stokes Law of fall of droplets.**—(1) *Empirical.* The experiments by which the value of the electronic charge was determined by the droplet method gave consistent results only when this law was modified by the factor $(1 + Al/a)$, where $l/a$ is the ratio of mean free path to radius of droplet. (2) *Hydrodynamic theory* gives as a first approximation $(1 + \xi/a)$, where $\xi$ is the coefficient of slip. (3) *Kinetic theory* gives $(1 + 0.7004l/a)$ in case all the molecules are diffusely reflected from the surface of the droplet, where $l$ is defined by the relation $\eta = .3502\rho\bar{c}l$. If, however, the fraction reflected diffusely is $f$, the fraction $(1 - f)$ being specularly reflected, then the factor is $[1 + 0.7004(2/f - 1)(l/a)]$. The theory developed by Cunningham gave the numerical constant as 0.79, but this value is too high since experimental values of $A$ nearly as low as 0.70 have actually been obtained.

**Coefficient of slip between gases and solids.**—(1) *Stokes' law method.* Since $\xi = Al$, $\xi$ may be computed directly from $A$. (2) *Rotating cylinder method* of determining viscosity is also capable of giving values of $\xi$ accurate to one per cent. If $\theta_0$ is the limiting deflection for high pressures, and $\theta$ the deflection for a low pressure, then $\xi$ for that low pressure is $(\theta_0 - \theta)/K$, where $K$ is a geometrical constant of the apparatus. Values obtained by this method agree closely with those obtained by the first method. (3) *Capillary effusion method.* If the rate of flow of gas for unit pressure difference is $T_0$ for high pressures and $T$ for a low pressure, then $\xi$ for that low pressure is $R(T - T_0)/4T_0$, where $R$ is the radius. (4) *Values of $\xi/l$ vary with the surface,* for instance from 0.70 for air-mercury, and 0.87 for air-oil and air-glass, to 1.07 for air-fresh shellac. They also *vary with the gas,* for instance from 0.81 for hydrogen-oil and 0.82 for $CO_2$-oil to 0.86 for air-oil, and 0.90 for helium-oil.

**Coefficient of diffuse reflection of gas molecules,** determined from the relation $A = (2\eta/\rho\bar{c})(2/f - 1)$ gives values of $f$ which *vary with the surface* from 0.79 for air-fresh shellac and 0.89 for air-glass to 1.00 for air-mercury. The values also *vary with the gas* from 0.87 for helium-oil and 0.895 for air-oil to 0.92 for $CO_2$-oil and hydrogen-oil. The values are for 23° C.

## 1. Introduction.

In 1911 [1] it was first shown that the so-called "oil-drop method" was capable of yielding not only a measurement of the electron, but also a determination of the "*coefficient of slip*" between a gas and the surface of a liquid or solid, which was of a sufficient degree of precision to justify the hope that it would be possible with its aid to settle definitely some of the interesting and important problems of the kinetic theory which had absorbed the attention of Maxwell, Kundt and Warburg and others half a century ago but which have been since then matters of dispute for the reason that the experimental technique of that day was insufficiently precise to permit of definitive conclusions. Since the results which have followed from a careful pursuit of these problems by the oil-drop method and by a new one quite as accurate which is presented herewith, are in some particulars at variance with a considerable amount of preceding work, some of it theoretical and some experimental, the theoretical considerations which are here involved will be quite fully restated for the sake of facilitating a critical analysis by others. An attempt will also be made to present the development of ideas in this field in its correct historical sequence.

## 2. The Oil-Drop Method of Measuring Slip.

If $e_n$ is the charge on a spherical particle falling first with speed $v_1$ under the influence only of the gravitational pull $mg$ and then rising against gravity with a speed of $v_2$ in a vertically directed electric field of strength $F$, the equation which is nothing more than the expression of the fact that the velocity of the particle is proportional to the acting force—a fact about which in the case of small enough drops there can not be the slightest uncertainty, since it has been rigorously and accurately proved both theoretically and experimentally—is

$$\frac{v_1}{v_2} = \frac{mg}{Fe_n - mg} \quad \text{or} \quad e_n = \frac{mg}{F}\frac{(v_1 + v_2)}{v_1}. \tag{1}$$

Equally certain may we be about the correctness of Stokes' hydrodynamical equation

$$X = 6\pi\eta a v, \tag{2}$$

provided it be assumed that the medium is homogeneous and that there is no slip between it and the surface of the sphere. Making this assumption, for the moment, and combining (2) with the equation expressing the relation between mass, density, and volume, viz.,

$$X = mg = \tfrac{4}{3}\pi a^3(\sigma - \rho)g, \tag{3}$$

[1] Physical Review, 32, 382, 1911.

there results at once the usual form of Stokes' law of fall, namely,

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho). \tag{4}$$

From 1, 3 and 4 there then follows at once

$$e_n = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{1}{g(\sigma - \rho)}\right)^{1/2}\frac{(v_1 + v_2)v_1^{1/2}}{F}, \tag{5}$$

which gives the charge upon the droplet in terms of the velocity $(v_1 + v_2)$ and otherwise accurately known quantities.

The most characteristic and most significant fact brought to light by the oil-drop method was that $(v_1 + v_2)$ could be made to take on a series of values constituting an arithmetical progression and having a greatest common divisor $(v_1 + v_2)_0$ which corresponds then to a charge of one electron upon the droplet, so that the equation

$$e_1 = \frac{4}{3}\pi\left(\frac{9\eta}{2}\right)^{3/2}\left(\frac{1}{g(\sigma - \rho)}\right)^{1/2}\frac{(v_1 + v_2)_0 v_1^{1/2}}{F} \tag{6}$$

is the value of the electronic charge provided only the assumptions made in (2) of homogeneity in the medium and no slip, are correct.

Now the fact which was brought to light as soon as these experiments were tried, in the fall of 1909, was that $e_1$ did not come out a constant when droplets of different rates of fall and therefore of different radii were used in air at atmospheric pressure; but, instead, while perfect consistency was obtained in working on different droplets having the same rate of fall, the larger (more rapidly falling) drops gave consistently smaller values of $e_1$ than did the smaller drops. Indeed the apparent value of $e_1$ pushed up quite continuously about 10 per cent as the times of fall per cm increased from 5 to 50 seconds. This clearly meant that the smaller droplets fell more rapidly than in accordance with the requirements of Stokes' law because, as they diminished in size, they began to fall, so to speak, more and more nearly freely between the holes of the medium, *i.e.*, between the molecules of the air.

However, at the time at which these experiments were first performed (in the fall of 1909) there was available no theoretical work whatever as to the correct law of motion of a spherical droplet through a gaseous medium, with which (2) might be replaced. The procedure followed therefore was to seek to obtain wholly empirically a correction term to Stokes' law which should take into account the inhomogeneities in the gaseous medium. Since the size of the inhomogeneities had the linear dimensions of the mean free path $l$, while the corresponding linear dimen-

sion of the drop had to be proportional to its radius $a$, the correction which was to be applied to Stokes' law had evidently to be a function of the argument $l/a$, and in order to fit the experimental data, or for that matter to satisfy obvious theoretical considerations, it had to be applied in such a way as to cause the speed to increase as $l/a$ increased. Therefore a corrected form of Stokes' law which would take into account any kind of increase in speed due to the gaseous inhomogeneities could clearly be written as follows:

$$X = 6\pi\eta a v \left\{ 1 + f\left(\frac{l}{a}\right) \right\}^{-1}, \tag{7}$$

for this simply adds to Stokes' law a correction term of unknown form in $l/a$ but in such a way as to make $v$ increase as $l/a$ increases. In the absence of information as to the form of $f(l/a)$ we could evidently express it, as pointed out in earlier papers, in terms of the undetermined constants $A$, $B$ and $C$, etc., by writing

$$f\left(\frac{l}{a}\right) = 1 + A\frac{l}{a} + B\frac{l^2}{a^2} + C\frac{l^3}{a^3}, \text{ etc.},$$

and *so long as attention is confined to sufficiently small departures from Stokes' law* it is clearly legitimate to neglect second-order terms in $l/a$ and therefore to write

$$X = 6\pi\eta a v \left\{ 1 + A\frac{l}{a} \right\}^{-1} \tag{8}$$

or

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{ 1 + A\frac{l}{a} \right\}. \tag{9}$$

Using this form of equation to combine with (1) and denoting now by $e$ the absolute value of the electron and by $e_1$, as above, the apparent value of this charge obtained from the use of (4) rather than of (9) there resulted at once

$$e\left(1 + A\frac{l}{a}\right)^{3/2} = e_1 \qquad \text{or} \qquad e^{2/3}\left(1 + A\frac{l}{a}\right) = e_1^{2/3}. \tag{10}$$

If then we knew $a$ for all of our droplets, since $l$ was known, we could obtain $e_1$ from (6) and then plot a curve connecting $l/a$ and $e_1^{2/3}$. It is clear too from the form of (10) that this curve would necessarily be a straight line so long as the observational data were confined to a region in which the neglecting of the higher terms in the expansion of $f(l/a)$ was legitimate. *How far this would be true could only be determined by examining the curve itself.* The slope of that straight line would then clearly be $A$ and the intercept of this line on the $e_1^{2/3}$ axis would be $e^{2/3}$.

In the preceding papers $e^{2/3}$ has been the sole object of concern, and the straightness of the line has been found to hold much farther than a most satisfactory determination of the value of the intercept demanded. In this paper, on the other hand, attention is directed solely to the constant $A$, to its accurate measurement and to its significance.

Since $l$ itself is incapable of precise evaluation, but since with a given gas it is always inversely proportional to pressure, I have in later papers preferred to write (10) in the form

$$e^{2/3}\left(1 + \frac{b}{pa}\right) = e_1^{2/3} \tag{11}$$

and then to plot $e_1^{2/3}$ against $1/pa$, thus determining the constant $b$ instead of $A$. With this procedure, by directly measuring $e_1^{2/3}$ for different drops at the same pressure, or for the same drop at different pressures, or both, and by plotting the different values of $e_1^{2/3}$ thus obtained against $1/pa$, it became possible to obtain $b$ (or $A$, since $A = b/pl$) wholly empirically, and thus to find by direct experiment and with much precision the law of fall which must replace Stokes' law when the droplets become so small that the inhomogeneities in the gaseous medium begin to cause that law to fail. *There could be no uncertainty about the correctness of this procedure if a and p were known with enough accuracy, and if the observational data were confined to a region close enough to that in which Stokes' law was found valid.* It was by this empirical procedure that the first term of the proper correction to Stokes' law of fall of a droplet of oil through air was finally found to have the exact numerical value given in (12),

$$X = 6\pi\eta av\left(1 + .864\frac{l}{a}\right)^{-1}, \tag{12}$$

provided that $l$ is defined by $\eta = .3502\rho\bar{c}l$. Also this law was found to be correct up to $l/a = .5$, at which point a second correction term to Stokes' law became necessary.

In the foregoing work in order to determine $a$ with any required degree of precision, the method of successive approximations was used. Thus the rigorously correct equations 1 and 3 (when reduced by the evaluation of the greatest common divisor of the speeds, so as to correspond to a single charge upon the drop) were solved for $a$, thus giving

$$a = \sqrt{\frac{3Fe}{4\pi g(\sigma - \rho)}\frac{v_1}{(v_1 + v_2)_0}} \tag{13}$$

and an approximately correct value of $e$ inserted in this equation. This gave, in view of the cube-root sign, a series of values of $a$ con-

taining errors of but one third that contained in the assumed value of $e$ and with which therefore a value of $e$ containing only a very minute error was obtained. With this new value of $e$ in turn a new series of values of $a$ containing only wholly inappreciable errors could be computed with the aid of (13) and the final value of $e$ then obtained from the intercept.

I have thus far shown merely how the constants $A$ and $b$ in (10) and (11) were empirically determined. But it remains to show what is their significance from the standpoint of the hydrodynamical concept of slip. In hydrodynamical theory the modified form of Stokes' law which takes into account surface slip [1] is

$$X = 6\pi\eta av \left\{ \frac{1 + 2\gamma}{1 + 3\gamma} \right\} \tag{14}$$

or

$$v_1 = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho)\left\{ \frac{1 + 3\gamma}{1 + 2\gamma} \right\}, \tag{15}$$

in which $\gamma$ is defined by the equation

$$\gamma = \frac{\eta}{a\epsilon} = \frac{\zeta}{a}, \tag{16}$$

$\epsilon$ being called *the coefficient of external friction*, and the ratio of the internal to the external coefficient of friction $\eta/\epsilon = \zeta$ being called *the coefficient of slip*.

If the last factor in (16) is expanded in powers of $\gamma$ into

$$1 + \gamma + 2\gamma^2 + 4\gamma^3, \text{ etc.},$$

then we may neglect powers of $\gamma$ higher than the first, provided $\gamma$ is kept sufficiently small. But $\gamma$ can be kept as small as we please so long as we confine attention to the region which has been under consideration in all which has preceded, namely the region in which Stokes' law is just beginning to break down because the medium is just beginning to be sufficiently inhomogeneous so that the phenomenon of slip is just beginning to appear. Then (15) becomes

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}(1 + \gamma), \tag{17}$$

which is identical with the empirical equation (9). It is thus seen that $\gamma = \zeta/a = Al/a$, that is, that

$$\zeta = Al. \tag{18}$$

In other words the oil-drop method of determining $e$, which consists in plotting a series of values of $e_1^{2/3}$ taken on different droplets at different

[1] See Basset's Hydrodynamics, Vol. II., p. 271.

pressures against $1/pa$, and finding the intercept on the $e_1^{2/3}$ axis, *i.e.*, finding the limit toward which $e_1^{2/3}$ tends as $pa$ becomes infinite, is simply equivalent to graphically reducing the medium to a condition of infinite pressure in which the holes (inhomogeneities) are all squeezed out, and in which therefore Stokes' hydrodynamical equation is rigorously valid. This removes all uncertainty from all of the equations upon which the determination of $e$ depends. It is of course assumed in the foregoing that the sole cause of slip in gases is found in molecular inhomogeneities, but if this were not true Stokes' unmodified law would not hold accurately in dense media *as it is found experimentally to do.*

*Similarly the slope of the $e_1^{2/3}$, $1/pa$ line close to the intercept, where the $\gamma$ of (17) is just as small as we please, must correspond to a region in which the hydrodynamical theory underlying Basset's equation is rigorously applicable and therefore where it is rigorously correct to identify $\gamma$ with $Al/a$ or $\zeta$ with $Al$.*

From the hydrodynamical theory of slip alone we should not expect an equation of the form of (17) to remain valid through a large range of values of $1/pa$, *i.e.*, far from the region in which Stokes' law is valid. But in the case of gases this theory is applicable only to very small values of $1/pa$ so that we need not be concerned because the $e_1^{2/3}$, $1/pa$ line is actually found to remain straight, and an equation of the form of (17) to hold for a surprisingly long range of values of $1/pa$. This is merely a fortunate circumstance which makes it possible to determine coefficients of slip between gases and liquids and gases and solids with much certainty and precision by the oil-drop method. Without this fortunate circumstance the precision of this method of measuring slip would be greatly impaired. The slope of the $e_1^{2/3}$, $1/pa$ line is indeed theoretically identifiable with slip only very close to the intercept with the $e_1^{2/3}$ axis, but since that slope is *in fact* constant up to very appreciable values of $1/pa$ we are not concerned, when determining slip by the oil-drop method, with whether the hydrodynamical theory of slip accounts for the length of this straight line or not; for we are well aware that the physical conditions underlying this hydrodynamical theory of slip are no longer satisfied near the upper end of this line.

To recapitulate then, we have proved that since the coefficient of slip $\zeta$ is equal to $Al$ and since from (12) $A$ for oil and air is .864 and $l$ at 23° and 76 cm for air is computed from $\eta = .3502\rho\bar{c}l$ to have the value .000009417 cm, the coefficient of slip between air at 23° C, 76 cm and oil is

$$\zeta_{\text{air } 23°,\ 76 \text{ cm}} = .864 \times .000009417 = 0.000008136. \qquad (19)$$

For drops of radii from .0001 cm up to .0006 cm which is about the range

with which we are practically concerned $\gamma = \zeta/a$ would have a value varying from 1/12 to 1/70, so that the complete justification for dropping higher powers of $\gamma$ than the first will be evident.

*The foregoing procedure may then be used with entire confidence for finding the coefficient of slip between any gas and a liquid or solid to which the oil-drop method of experimentation is applicable.*

### 3. The Kinetic Theory of Slip in Gases.

But there is an altogether general relation between the coefficient of slip and the law of reflection of gaseous molecules which may be obtained as follows.

To begin with the simplest possible case, assume a gas streaming slowly through a tube and let it be assumed at first that the gaseous molecules impinging upon the surface of the tube are "diffusely reflected," *i.e.*, are wholly absorbed and later reëmitted so that the direction of exit of a molecule from the surface bears no relation whatever to its direction of impact upon the surface. Familiar kinetic-theory considerations show that the number $n$ of molecules impinging per second upon 1 square centimeter of surface in a gas at rest is given by

$$n = \tfrac{1}{4} n\bar{c}, \tag{20}$$

in which $n$ is the number of molecules per c.c. and $\bar{c}$ is their average velocity of agitation. This is a perfectly general relation quite independent of the validity of any particular law of distribution of molecular velocities, and the error due to slow streaming motion is negligible.

If now the impinging molecules be assumed to have an average or mass motion parallel to the surface of velocity $v$ (which is exceedingly small compared to $\bar{c}$), then obviously the tangential momentum communicated to the wall per second by the impact of the $\frac{1}{4} n\bar{c}$ molecules upon it is

$$\tfrac{1}{4} n\bar{c}mv, \tag{21}$$

but if the *impinging* molecules have the average tangential velocity $v$, since the *layer of the gas* which is next to the surface is made up half of molecules entering that surface with the tangential velocity $v$, and half of molecules leaving that surface with the average tangential velocity which, according to our assumption, is zero, the *average* tangential velocity $v_0$ of the layer of gas next the wall is given by $v_0 = v/2$ and the expression for the tangential momentum given to the wall per second per square centimeter in terms of this mean velocity of the surface layer of gas is $\frac{1}{2} nm\bar{c}v_0$. But this expression, which is equal to the tangential force in dynes acting on each square centimeter, when it has been divided by $v_0$, is, by definition, the coefficient of external friction $\epsilon$ so that we have

$$\tfrac{1}{2} nm\bar{c} = \epsilon. \tag{22}$$

Therefore the coefficient of slip is given by

$$\zeta = \frac{\eta}{\epsilon} = \frac{.3502nm\bar{c}l}{.5nm\bar{c}} = .7004l,^{1} \tag{23}$$

or since $l$ when computed from the equation used above, namely $\eta = .3502nm\bar{c}l$, is at 23° C, 76 cm .00009417, *the numerical value of the coefficient of slip between air at* 23°, 76 *cm and a surface which reflects its molecules wholly "diffusely" is given by*

$$\xi_{(\text{air } 23°,\ 76)} = .7004 \times .00009417 = .000006595. \tag{24}$$

*The fact that this is considerably less than the observed value of the slip found in* (19) *can only mean that the assumption of diffuse reflection is incorrect in the case in hand: namely air and oil. This result furnishes the complete justification for Maxwell's introduction of the coefficient f* which he defined as the fraction of the total number of impinging molecules which are "absorbed and afterwards evaporated," [2] the fraction $(1 - f)$ being then taken as the portion which is specularly reflected. The existence of this fraction $f$ merely means that there is a measurable tendency for molecules which impinge at a given angle upon the surface in question to be reflected so as to make the angle of incidence equal to the angle of reflection, and that the actual distribution of reflected molecules, all of which are incident at a given angle, can be *reproduced* by mixing a fraction $f$ of diffusely reflected molecules with a fraction $1 - f$ of specularly reflected molecules. The theoretical evaluation of Maxwell's $f$ from the measured coefficient of slip may be made, in accordance with the mode of approach used above, as follows.

If only the fraction $f$ of the *impinging* molecules is absorbed, the momentum communicated to the wall, in terms of $f$ and the average tangential velocity $v$ of all the impinging molecules, is

$$\tfrac{1}{4}mn\bar{c}fv. \tag{25}$$

But the average tangential velocity $v_0$ of the *surface* layer of molecules, since it is made up of $\frac{1}{4}n\bar{c}$ impinging molecules of tangential velocity $v$, and of $\frac{1}{4}n\bar{c}(1 - f)$ returning molecules, also of tangential velocity $v$, and of $\frac{1}{4}n\bar{c}f$ returning molecules of tangential velocity zero, and since the total number of molecules in this layer is the sum of those going in

[1] This is precisely the result obtained by Kundt and Warburg (Pogg. Ann., 155, p. 547, and 159, p. 401, 1876), and by Maxwell, Scientific Papers, Vol. II., p. 709, save that these authors used slightly different value of the constant .3502. This, however, does not change the numerical value of the slip, if only the same constant is used as, of course, it should be in the evaluation of $l$.

[2] Maxwell, Scientific Papers, Vol. II., p. 705.

and those coming out, namely $\frac{1}{2}n\bar{c}$, is given by

$$v_0 = \frac{\{\frac{1}{4}n\bar{c} + \frac{1}{4}n\bar{c}(1-f)\}v + \frac{1}{4}n\bar{c}f \times 0}{\frac{1}{2}n\bar{c}};$$

$$\therefore \quad v_0 = \left(1 - \frac{f}{2}\right)v \qquad \text{or} \qquad v = \frac{v_0}{\left(1 - \frac{f}{2}\right)} \tag{26}$$

Substituting this value of $v$ in (25) and then writing the definition of $\epsilon$, namely

$$\frac{1}{4}mn\bar{c}f \frac{v_0}{\left(1 - \frac{f}{2}\right)} = \epsilon v_0 , \tag{27}$$

there results

$$\zeta = \frac{\eta}{\epsilon} = \frac{.3502mn\bar{c}l}{\frac{1}{4}mn\bar{c}\left(\frac{f}{1 - \frac{f}{2}}\right)} = .7004l\left(\frac{2}{f} - 1\right)^1 \tag{28}$$

or since

$$\zeta = Al, \qquad f = \frac{1.4008}{A + .7004}. \tag{29}$$

Inserting in (29) the observed value of $A$ for air and oil at 23° C, 76 cm, viz., .864, we obtain

$$f = .895.$$

*Therefore, when the molecules of air impinge upon oil at a given angle, 89½ per cent of the impinging molecules are diffusely reflected (absorbed and reëmitted) and 10½ per cent are specularly reflected.* The foregoing method of finding $f$ should be altogether valid so long as $2/f$ is not very large in comparison with unity. As $f$ approaches zero, however, $\zeta$ becomes large and the procedure used in reducing (15) to (17) becomes invalid.

## 4. Significance of Variations in $A$ with the Nature of the Gas.

Although equations (28) and (29) appear to involve the assumption that the constant $k$ of the viscosity formula $\eta = k\rho\bar{c}l$ has the value .3502, the value of $f$ obtained from the use of (28) is quite independent of any assumption whatever as to the value of $k$ provided only that in the computation of $A$ from

$$\zeta = \frac{b}{p} = Al$$

the value of $l$ used is obtained from $\eta = .3502\rho\bar{c}l$ as it should be. That

[1] This form again is the same as that found by Maxwell, see Scientific Papers, Vol. II., p. 709, save for the use of 1/3 by him in place of .3502.

this is true may be seen by writing (23) and (28) in the forms

$$\zeta_0 = \frac{\eta}{\epsilon} = \frac{2\eta}{\rho\bar{c}} = \frac{2k\rho\bar{c}l}{\rho\bar{c}} = 2kl \tag{30}$$

and

$$\zeta_f = 2kl\left\{\frac{2}{f} - 1\right\}. \tag{31}$$

From which

$$\zeta_f = \zeta_0\left\{\frac{2}{f} - 1\right\}$$

or

$$f = \frac{2\zeta_0}{\zeta_f + \zeta_0}, \tag{32}$$

in which $\zeta_0$ is seen from (30) to have the value $2\eta/\rho\bar{c}$, an expression quite independent of $k$ and all of whose terms are accurately known. This shows that if we have any means whatever of measuring $\zeta_f$ we may substitute the measured value in (32) and solve for $f$.

Now the oil-drop slope $b/p$ is a direct measure of $\zeta_f$ since we had $\zeta_f = b/p = Al$. Also since $\zeta_0 = A_0 l$, $\zeta_0$ being assumed to be measured with the same gas on a perfectly diffusing surface, it will be seen from (30) and (32) that

$$f = \frac{2\zeta_0}{\zeta_f + \zeta_0} = \frac{2A_0}{A + A_0} = \frac{4k}{A + 2k}. \tag{33}$$

But since $A$ is obtained from the slope $b/p$ by means of

$$A = \frac{b}{pl} = \frac{b}{p}\frac{k\rho\bar{c}}{\eta} \tag{34}$$

we have

$$f = \frac{4k}{A + 2k} = \frac{4k}{\frac{bk}{p}\frac{\rho c}{\eta} + 2k} = \frac{4}{\frac{b}{p}\frac{\rho\bar{c}}{\eta} + 2}. \tag{35}$$

Thus $f$ is a constant for different gases if $(b/p)(\rho\bar{c}/\eta)$ is a constant; also if $(b/p)(\rho\bar{c}/\eta)$ is constant, then this expression multiplied by any quantity whatever which is *assumed* to be the same for all gases (as was the $k = .3502$ used above) is also a constant.

Hence if $A$ in (9) and (10) is found to come out a constant for different gases $f$ is also the same for the different gases, and if $A$ varies from gas to gas $f$ also varies. *In other words the present experiments throw no new light whatever upon the proper value of the kinetic theory constant k but they are altogether unambiguous in their significance as to f.*

## 5. The Correct Form of the First Order Correction Term to Stokes' Law of Fall.

We are now in position to obtain the general form of the first order correction term to Stokes' law. For since (17) rests upon an unimpeachable hydrodynamical basis so long as $\zeta/a$ is small and since in (17) we have proved that for this case

$$\gamma = \frac{\zeta}{a} = \frac{Al}{a}$$

and also that in general

$$\zeta = .7004l\left(\frac{2}{f} - 1\right), \tag{36}$$

it follows that the correct numerical form of the equation which should replace Stokes' law when $l/a$ becomes so large that this law just begins to fail is

$$X\left\{1 + .7004\left(\frac{2}{f} - 1\right)\frac{l}{a}\right\} = 6\pi\eta av$$

or

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\eta}\left\{1 + .7002\left(\frac{2}{f} - 1\right)\frac{l}{a}\right\}. \tag{37}$$

It is interesting to compare this equation with that deduced from purely theoretical considerations by Cunningham [1] in 1910, in which the correction term to Stokes' law takes the form [2]

$$1 + \frac{1.63\frac{l}{a}}{1 + f} \tag{38}$$

It is not at all surprising that this does not agree with (37) when $f = 0$, for, as indicated above, (37) could not hold for that case anyway—a case of no practical interest since nothing like it occurs in nature. But it *is* significant that for the case of diffuse reflection ($f = 1$) Cunningham's numerical coefficient is .815 when (36) indicates that it should be .7004. The discrepancy is not quite so bad when Cunningham's equation is freed from a slight error which, as I pointed out in a footnote in Physical Review, 32, 380, 1911, crept into it because of a confusion of $\bar{c}$ with $\sqrt{\bar{c}^2}$. When this error is eliminated and when $l$ is obtained, as in all the foregoing from $\eta = .3502p\bar{c}l$, the numerical coefficient in that equation becomes .788 instead of .815. But even this is more than 10 per cent higher than it should be if (37) is valid.

[1] Cunningham, Proc. Roy. Soc., Series A, Vol. 83, p. 360, 1910.

[2] The notation used by Cunningham in his paper is the reverse of that introduced by Maxwell, $f$ and $1 - f$ being interchanged. The form in (38) is Cunningham's when reduced to Maxwell's notation.

It was because of this discrepancy that I undertook two rather elaborate series of experiments designed to test in wholly independent and different ways the validity of equation (37) and the interpretation which has been placed upon the divergence between the numerical constants in (19) and (24).

### 6. Oil-Drop Tests of Equation (37).

The first definite experimental evidence which was found in favor of the correctness of (37) came when the nature of the droplet was changed without changing the nature of the gas. Thus, the curves labelled I., III. and IV. in Fig. 1 represent measurements made in air upon droplets

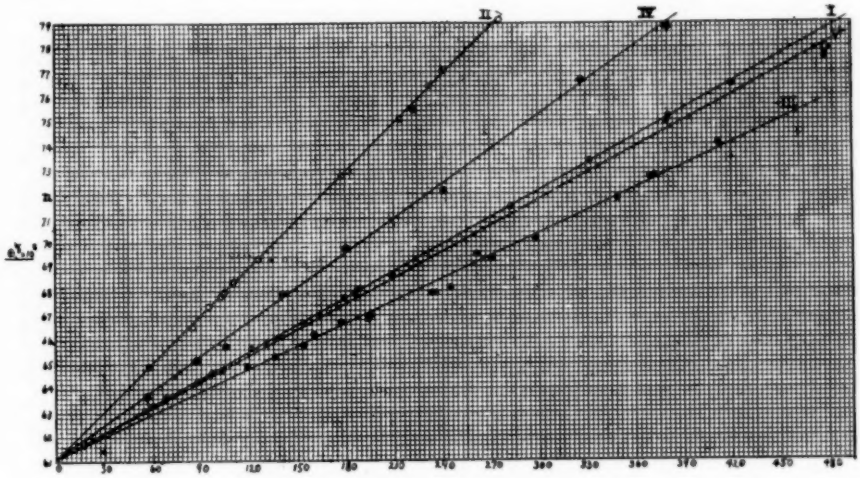

Fig. 1. $e_1^{2/3} \times 10^8$ as a function of $1/pa$.

of oil, mercury and shellac respectively. The values of $A$ for these three lines are .842, .708, and 1.078 respectively and the corresponding values of $\zeta_{23°.76}$ are .00000793, .00000667, and .0000101.

Although, under the conditions prevailing at the time these experiments were made, the error in the slopes may possibly be as much as 3 per cent (indeed the value of $A$ for air-oil is here 2.5 per cent lower than my most reliable determination, Phil. Mag., Vol. XXIX., p. 12, 1917, which reduced the probable error in $A$ to about 1 per cent) yet the differences between these slopes are so large as to leave open no escape from the conclusion *that the nature of the surface exerts a very important influence upon A and therefore upon the tendency of the molecules to be specularly reflected.*

It is very interesting, too, to observe that the value of $A$ for air-mercury, namely .708, has practically reached the lowest limit permitted

by (37) which in the case of diffuse reflection ($f = 1$) is seen to be .7004. This observed value is more than 10 per cent lower than the lowest possible value permitted by Cunningham's equation.

I am disposed to connect the attainment of diffuse reflection in the case of droplets of mercury with the powerful molecular (cohesive) field possessed by this substance. This would result in the condensation and reëvaporation of the surrounding gas—a condition which is equivalent to diffuse reflection as the latter term is used by Maxwell.

The organic substances oil and shellac might be expected to have very much weaker molecular fields and to condense the gas much less completely than mercury, as they are in fact here seen to do. It is possible, however, that the cause of the low value of $A$ for mercury is to be found rather in the roughening of the surface by oxidation than in the high value of the molecular constant. I have found no substance which shows a higher value of $A$ than does fresh shellac.

But again Fig. 1 also shows that the nature of the gaseous molecule as well as the nature of the reflecting surface may exert an influence upon the tendency to specular reflection. For curve II (Fig. 1) represents a series of experiments which I made on oil drops in hydrogen. This slope, when divided by the ratio of the mean free paths of the molecules of hydrogen and air, namely 1.845, is shown in the dotted line labelled V. It is 3.3 per cent lower than the value of the slope for the air-oil line, *i.e.*, it gives for hydrogen-oil $A = .815$ against .842 found in this experiment for air-oil and .864 which I regard as the correct value for this combination. The difference is considerably larger than the estimated observational error. The evidence is then fairly good that *hydrogen shows a slightly larger tendency to specular reflection on oil than does air.* Also according to the best measurement on $CO_2$ and oil, the value of $A$ for this combination is close to .82. Three different observers, working with my apparatus, have found it about 4 per cent lower than $A$ for air-oil.

### 7. Coefficients of Slip by the Rotating Cylinder Method.

In view of the importance of checking the foregoing results by a wholly independent method a new series of slip-determinations was planned by the constant deflection method. So far as I know, this method has not been used heretofore for slip-determinations, but it is, I think, the most accurate method which is available. The theory of the method is as follows.

In the constant deflection method of measuring the viscosity of a gas, if the inner torsionally suspended cylinder has a radius $a$ (Fig. 2) and a

length $L$ and the outer rotating cylinder a radius $b$, and if $\omega$ is the constant angular velocity of the layer of gas at any radius between $a$ and $b$, then the torsional moment $\overline{Fr}$ due to the viscous drag acting on the cylindrical surface of gas of radius $r$ is given by

$$\overline{Fr} = 2\pi r^3 L\eta \frac{\partial \omega}{\partial r}. \tag{39}$$

Fig. 2.

If now we assume *no slip* at either of the surfaces $a$ or $b$ and therefore integrate $\omega$ between the limits o and the angular velocity of the external cylinder $\omega_2$ we obtain, since in the steady state $\overline{Fr}$ is not dependent on $r$,

$$\overline{Fr} \int_a^b \frac{\partial r}{r^3} = 2\pi L\eta \int_0^{\omega_1} \partial\omega \tag{40}$$

or

$$\overline{Fr} = 4\pi L\eta \frac{a^2b^2}{b^2 - a^2} \omega_1. \tag{41}$$

Replacing $\overline{Fr}$ by $\pi^2 I\theta/t^2$, where $\theta$ is the constant angular deflection of the inner cylinder, $I$ its moment of inertia and $t$ its half period in vacuo, we obtain the well-known characteristic formula of the constant deflection method, viz.:

$$\eta = \frac{\pi I\theta(b - a)(b + a)}{4t^2 La^2b^2\omega_1}. \tag{42}$$

In order now to modify this analysis so as to take account of slip between the surface of the gas and that of each cylinder $a$ and $b$ we must integrate the $\partial\omega$ in (39) and (40) not between o and $\omega_1$, but rather between $\omega_a$ and $\omega_b$, these symbols representing the angular velocities of the layers of gas in contact with $a$ and $b$ respectively. We thus obtain, instead of (41),

$$\overline{Fr} = 4\pi L\eta \frac{a^2b^2}{b^2 - a^2} [\omega_b - \omega_a]. \tag{43}$$

But now, by definition of the coefficient $\epsilon$ of external friction, if $f$ is the tangential force acting between the surface of the inner cylinder and $v_0$ the difference in linear velocity between the surface of the cylinder $a$ and the layer of gas in contact with it, then

$$f = 2\pi aL\epsilon v_0' \tag{44}$$

or

$$fa = \overline{Fr} = 2\pi a^2 L\epsilon v_0; \tag{45}$$

substituting in this equation the value of $v_0$ obtained from $\omega_a = v_0/a$

we obtain

$$\omega_a = \frac{\overline{Fr}}{2\pi a^3 L\epsilon}. \tag{46}$$

Precisely similarly, if $f'$ is the tangential force on $b$ and $v_0'$ the difference in linear velocity between the surface of $b$ and the gas in contact with it, we have

$$f'b = \overline{Fr} = 2\pi b^2 L\epsilon v_0' \tag{47}$$

and

$$\omega_b = \omega_1 - \frac{v_0'}{b} = \omega_1 - \frac{\overline{Fr}}{2\pi b^3 L\epsilon}. \tag{48}$$

The substitution of (46) and (48) in (43) gives, after the insertion of

$$\overline{Fr} = \frac{\pi^2 I\theta}{t^2}$$

and also of the definition $\eta/\epsilon = \zeta$,

$$\eta = \frac{\pi I(b-a)(b+a)\theta}{4t^2 La^2b^2\omega_1}\left[1 + 2\zeta\frac{a^3+b^3}{ab(b^2-a^2)}\right]. \tag{49}$$

If now we denote by $\eta_a$ the *apparent* value of the viscosity obtained by the use of (42) and by $\eta$ the real value obtained by the use of (49) and if for brevity we write

$$\frac{2(a^3+b^3)}{ab(b^2-a^2)} = K \tag{50}$$

we obtain from (42) and (49)

$$\zeta = \left(\frac{\eta}{\eta_a} - 1\right)\frac{1}{K}. \tag{51}$$

For the practical application of this formula it is of course only necessary, if the speed of rotation of the outer cylinder is always kept constant, to measure the deflection $\theta$ at a relatively high pressure where $\zeta$ $(= .7004l)$ is so small that the second term in (49) is wholly negligible, and then to reduce the pressure until $\theta$ has attained a measurably smaller value $\theta'$. The slip coefficient for this lower pressure is then given very simply by

$$\zeta = \left(\frac{\theta}{\theta'} - 1\right)\frac{1}{K}. \tag{52}$$

The accuracy with which, under the best attainable experimental conditions, $\theta$ can be determined by this method being about one part in two thousand, it should be possible to have a difference between $\theta$ and $\theta'$ of but 5 per cent and still to secure an accuracy in the determination of $\zeta$ of about 1 per cent. *This makes the determination of coefficients of slip*

*a matter of real precision* and permits the definite settlement of questions left altogether unsettled by the cruder methods of the earlier observers. Under the somewhat imperfect working conditions used below the uncertainty in $\zeta$ is however from two to three per cent for air, and somewhat more for $CO_2$.

## 8. The Comparison of Results by the Two Methods.

The following papers by Messrs. Stacy and Van Dyke will show not only how satisfactorily the foregoing results, both theoretical and experimental, are checked by the application of this method, but also how well the personal equation has now been eliminated by the agreement between the results of different observers working at different times and under somewhat different conditions.

The final results obtained to date by the constant deflection method may be briefly summarized as follows:

I. When the surfaces of the cylinders had just been machined so that, when looked at from the eyes of a molecule, they were essentially rough surfaces, capable only of throwing back the molecules diffusely, the coefficient of slip between this surface and air, reduced to 23°, 76 cm, was found by Mr. Stacy to be $\zeta = .000006615$ as against my limiting theoretical value (see 24) $\zeta = .000006595$. *In other words the value of A for this surface had practically the theoretical limit* $A = .7004$ *demanded by* (37).

II. When the cylinder surfaces were then covered with shellac and dried the value of the slip, reduced to 23°, 76 cm, at once increased to .0000097 which corresponds, since $\zeta = Al$, to $A = 1.03$. This, in view of the inconstancy in $A$ for shellac, to be immediately considered, is in altogether satisfactory agreement with the value shown in Fig. 1, IV which, it will be remembered, was $A = 1.07$.

III. When the shellaced surfaces were allowed to stand for several days they showed a continually diminishing value of $A$ (due, I think, to slow oxidation) which according to Mr. Stacy's observations reached in two months the figure $\zeta = .00000677$, only $2\frac{1}{2}$ per cent higher than the theoretical limit corresponding to diffuse reflection. Precisely the same sort of a slow change in $A$ with shellac has been found as detailed in Mr. Stacy's paper by an independent observer Mr. Harrington.

IV. The observations on Mr. Stacy's old shellac surface, interrupted in 1918 by his and by the author's participation in the war, were taken up again two years later by Mr. Van Dyke who obtained a mean value $\zeta = .0000068$ in complete agreement with Mr. Stacy.

V. Mr. Van Dyke did not find it possible, by cleaning off the shellac

from the cylinders, to restore completely their original diffusely reflecting quality, the mean value of $\zeta$ for the cleaned brass surface remaining at .0000075. By scratching the surface with sandpaper $\zeta$ was reduced to .00000728. The inability to restore completely the surface to the condition of perfect roughness, after the treatment it had received, is not surprising. Had the observed change been in the other direction the result would have been disturbing for the theory, for *only by making the surface so rough that molecular mountain peaks, so to speak, project far up into the streaming gas, and thus rendering the consideration of anything like a surface layer of gas altogether impossible, could the drag be made larger than that corresponding to diffuse reflection.* This condition could probably be realized with a granular surface like that produced by smoke or by an electrolytic deposit.

VI. I asked Mr. Van Dyke next to coat the cylindrical surfaces with the same clock-oil with which I had obtained the value $A = .864$ or the slip $\zeta = .00000814$. The slip at once rose to the mean value .00000818 *in excellent agreement with results of the oil-drop method.*

VII. Mr. Van Dyke then used $CO_2$ gas with his oiled cylinders and got a value of $A$ distinctly lower than for air, viz., .813, also in complete agreement with the results of the oil-drop method, which had yielded in $CO_2$ $A = .82$, *thus fortifying the validity of the conclusion that the nature of the gaseous molecule as well as the nature of the surface has a measurable influence upon the tendency to specular reflection* (*Maxwell's f*).

## 9. *A* and the Coefficient of Slip for Glass and Air.

I have made no measurements upon the coefficient of slip between glass and air; but there is evidence that it has a value exceedingly close to that between oil and air. Thus Warburg [1] by reducing the pressure, in viscosity determinations with glass capillaries, until slip began to be observable, obtained, from his only recorded measurement with his capillary No. I., $\zeta_{15°,\ 3.38\ mm} = .00017$ which reduces to

$$\zeta_{15°,\ 76\ cm} = .0000076.$$

From his recorded measurements with capillary No. II. he obtained

$$\zeta_{15°,\ 3.9\ cm} = .00016 \quad \text{and} \quad \zeta_{15°,\ 3.38\ cm} = .00018.$$

These measurements reduce to

$$\zeta_{15°,\ 76\ cm} = .0000082 \quad \text{and} \quad \zeta_{15°,\ 76\ cm} = .0000080.$$

Giving all these three determinations equal weight we obtain

$$\zeta_{15°,\ 76\ cm} = .00000793,$$

[1] Pogg. Ann., 159, p. 401, 1876.

which reduces when the temperature correction is made to

$$\zeta_{23°,\ 76\ \mathrm{cm}} = .00000822.$$

This is quite close to the value for oil and air given in (19), namely $\zeta$ 23°, 76 cm = .00000814.

The only other careful work by the capillary tube method from which I have been able to compute $\zeta$ for air and glass is that by Knudsen.[1] According to the following analysis of this data it yields a value of $\zeta$ for glass and air very close to the value found by Warburg.

Knudsen writes Poiseuille's equation, uncorrected for slip, in the form

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}p,$$

in which $T$ is the quantity of gas, measured by the product of pressure and volume, which is driven per second through a capillary of length $L$ and radius $R$ by a pressure-difference of 1 dyne per sq. cm and $p$ is the average pressure at the two ends, *i.e.*, $(p_1 + p_2)/2 = p$. Poiseuille's law, corrected for slip, then becomes

$$T = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}\left(1 + \frac{4\zeta}{R}\right).$$

Knudsen further measures the outflow through capillary tubes for a great range of mean pressures down to very low ones and represents all his results by the empirical formula

$$T = ap + \beta\frac{1 + c_1 p}{1 + c_2 p}$$

and evaluates the constants $a$, $b$, $c_1$, $c_2$ by means of his experimental data.

For such values of $c_1 p$ and $c_2 p$ as we are here concerned with 1 is negligible in comparison with this product and Knudsen's empirical equation becomes

$$T = ap + b\frac{c_1}{c_2}.$$

For sufficiently large values of the pressure this reduces, as it should, to $T = ap$ and from Poiseuille's equation we see that

$$a = \frac{\pi}{8}\frac{1}{\eta}\frac{R^4}{L}.$$

If now, as in the case of Warburg's experiments, we let $T'$ represent the apparent value of $T$ if there were no slip, while $T$ represents the real

[1] Knudsen, Ann. der Physik, 28, p. 117, 1909.

value, we have

$$\frac{T}{T'} = \left\{1 + \frac{4\zeta}{R}\right\}.$$

Hence

$$\frac{4\zeta}{R} = \frac{b\frac{c_1}{c_2}}{ap}$$

and

$$\zeta = \frac{Rb\frac{c_1}{c_2}}{4ap}.$$

We are therefore in position to compute the value of $\zeta_{76}$ from the values of $R$, $b$, $c_1/c_2$ and $a$ given by Knudsen for any of the tubes and gases which he uses. The results are of course quite independent of his theory and dependent only upon the ability of his constants $R$, $b$, $c_1/c_2$ and $a$ to reproduce the experimental $T$, $p$ curve, in the region of pressures with which we are here interested, which is limited to the region in which Poiseuille's law is just beginning to break down because of the appearance of the phenomenon of surface-slip. This is the only region in which we are here concerned with Knudsen's experimental data.

Knudsen does not make experiments upon glass and air, but since $\zeta$ for different gases is proportional to $l$ save as the nature of the gas modifies Maxwell's $f$, and since this last effect is only just measurable at best we may compute $\zeta$ for air and glass from his data taken with $H_2$, $O_2$, and $CO_2$ by multiplying by the ratio of mean free paths.

Utilizing in this way all the data taken by Knudsen (see Table II., p. 116, l.c.) except that on $H_2$ with tube No. 1., which I discard because Knudsen himself calls it unreliable, and all the data with tube No. 4, which I discard because it was a bundle of 24 tubes but 2 cm long and .00333 cm radius for which $\zeta$ comes out about 20 per cent higher than for any of the other tubes, presumably because the dimensions of such exceedingly minute capillaries can be determined with but little certainty, we obtain the following set of values of $\zeta$ for air at 25°, 76 cm.

| | |
|---|---|
| Tube No. 1 (using $O_2$), air | .00000816 |
| " " 1 ( " $CO_2$), air | .00000784 |
| " " 2 ( " $H_2$), air | .00000855 |
| " " 3 ( " $CO_2$), air | .00000876 |
| Mean | .00000828 |

When reduced to temperature 23° C this gives

$$\zeta_{23°,\,76} = .00000821,$$

which is seen to be identical with Warburg's value, although the uncertainty in both these determinations is doubtless as much as 5 per cent.

*The foregoing analysis appears to show then that $\zeta$ and $A$ for glass and air are practically identical with $\zeta$ and $A$ for oil and air for which my values are*

$$\zeta_{23°.76} = .0000082,$$
$$A = .864.$$

## 10. Numerical Values of Maxwell's $f$.

A condensed summary of the whole of this work may be made by computing with the aid of equation (29) and observed values of $\zeta$, or of $A$, the values of Maxwell's $f$ for the different gases and surfaces with which we have experimented.

For air and oil all observers and both methods are in excellent agreement, my value using oil drops being $A = .864$, Ishida's independent determination with my apparatus yielding $A = .862$ and Van Dyke's observations with the rotating cylinder giving $\zeta = 81.8 \times 10^{-7}$, which when combined with the value of $l$, viz., $94.17 \times 10^{-7}$, with the aid of $\zeta = Al$ gives $A = .868$. The mean of the three determinations is $A = .8647$ and this value is taken for the computation of $f$ from (29.)

For $CO_2$ and oil the different observers are in less satisfactory agreement probably because of the difficulty of duplicating exactly conditions as to purity of the gas. Dr. LaSalle obtained with my oil-drop apparatus $A = .825$. Mr. Eglin in very recent and very careful experiments with $CO_2$ has obtained $A = .820$. Dr. Ishida[1] with the same apparatus obtained .840 and Mr. Van Dyke's $\zeta = 50.0 \times 10^7$ by the rotating cylinder method reduces, since for $CO_2$ $l = 61.5 \times 10^7$, to $A = .813$. The mean of all these determinations, giving Van Dyke's and Eglin's data double the weight of the others since they ought to be the more precise, is $A = .823$ which is probably not in error by more than a per cent.

For hydrogen-oil my value of $A$ is .815 while Dr. Ishida's value obtained with my oil-drop apparatus is .811. The mean of the two, viz., $A = .813$, has been taken for the computation of $f$.

The monatomic gas helium shows according to Dr. Ishida's determination a higher value of $A$ than any other gas used with oil. There is as yet no other observation with which to compare it and $f$ is therefore computed from Ishida's $A = .901$.

All of the observations made with oil drops in different gases show that, as was to have been expected, the character of the gas has but little influence upon the character of the reflection, though the observed differ-

[1] Ishida regards his accuracy in the case of $CO_2$ as less than in the case of any other gas as he worked hastily and used but ten drops.

ences in $A$ are apparently considerably greater than the observational error.

TABLE.

*Values of Maxwell's f for Different Surfaces and Gases.*

| | $A$. | $f$ = Per Cent Diffuse Reflection at 23° C. | $1-f$ = Per Cent Specular Reflection at 23° C. |
|---|---|---|---|
| Air, $CO_2$, machined brass surface or old shellac surface | .70 | 100 | 0 |
| Air-mercury | .70 | 100 | 0 |
| Air-oil | .864 | 89.5 | 10.5 |
| $CO_2$-oil | .823 | 92 | 8 |
| Hydrogen-oil | .813 | 92.5 | 7.5 |
| Air-glass (Warburg-Knudsen) | .872 | 89 | 11 |
| Helium-oil | .901 | 87.4 | 12.6 |
| Air-fresh shellac | 1.07 | 79 | 21 |

NORMAN BRIDGE LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
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# A DETERMINATION BY THE CONSTANT DEFLECTION METHOD OF THE VALUE OF THE COEFFICIENT OF SLIP FOR ROUGH AND FOR SMOOTH SURFACES IN AIR.

By Leland Johnson Stacy.

Abstract.

**Coefficient of slip for rough and smooth surfaces in air, determined by the constant deflection method.**—The apparent coefficient of viscosity measured by this exceptionally precise method does not come out constant for the lower pressures unless correction is made for the slip at the surfaces. The relation $\eta_p'(1 + k\zeta_p) = \eta$ = constant, between $\eta_p'$, the apparent viscosity coefficient, and $\zeta_p$, the coefficient of slip, enables $\zeta_p$ to be determined from measurements of $\eta_p'$ at pressures of 0.2 mm or lower. The apparatus included a vacuum-tight chamber inside which a cylinder of radius 5.341 cm was suspended by a steel wire concentric with a cylinder of radius 6.063 cm which could be rotated at a constant slow rate so as to cause a steady deflection of the inner cylinder. The accuracy of this method of measuring $\eta_p'$ is so great that the values of $\zeta_{76} = \zeta_p p/76$ all lie within $\pm 4$ per cent of the mean. The chief difficulty was in keeping the air pure because of the gradual evolution of gas, probably hydrogen, inside the apparatus; but by taking observations only shortly after evacuation this effect was avoided. *For brass surfaces*, $\zeta$, reduced to 23° and 76 cm, came out $66.15 \times 10^{-7}$ which is practically the theoretical minimum deduced by Millikan for a completely diffusing surface, $65.9 \times 10^{-7}$. *For surfaces coated with shellac*, the coefficient was found to be $97 \times 10^{-7}$ for a fresh surface, in agreement with the value obtained by Lee from droplet measurements, but it decreased steadily with time, presumably because of a roughening due to oxidation, falling in two months to within 3 per cent of the theoretical minimum. The early part of this work was done in collaboration with E. L. Harrington.

**Coefficient of viscosity of air at 0.1 mm** is the same as at atmospheric pressure when correction is made for the slip effect. The constancy of the values obtained for $\zeta$ provides new evidence that the coefficient is independent of the pressure.

## I. Historical Development of the Idea of Slip.

THE theory that the coefficient of viscosity of a gas should be independent of the pressure was first deduced by Maxwell [1] from a consideration of the internal friction of molecules assumed to be rigid spheres. He first deduced the relation

$$\eta = \rho \bar{c} l, \tag{1}$$

where $\eta$ = coefficient of viscosity; $\rho$ = density of the gas; $\bar{c}$ = mean

[1] Phil. Mag., 1860, Vol. 19, p. 31.

molecular velocity; $l$ = mean free path of gas molecule. Since the density is directly proportional to the pressure, while the mean free path is inversely proportional to the same quantity, the product $\rho l$, and therefore $\eta$, should be independent of the pressure.[1] In a later paper,[2] Maxwell reported some experimental tests of his theory for pressures ranging from 30 in. to 0.5 in. of mercury. His apparatus consisted of a torsion pendulum of three plane-parallel plates suspended by an elastic fiber between four fixed plane-parallel plates. The whole system was enclosed in an airtight vessel and the logarithmic decrement of the oscillations was observed for different pressures. He found no observable change in the decrement, which is a measure of the viscosity, within the pressure range studied.

The same relation (1) was derived later by O. E. Meyer.[3] By an experimental arrangement similar to Maxwell's he checked the theoretical deductions for the same range of pressures. Results at pressures below 1/60 atmosphere showed a falling off of the viscosity coefficient, which he later ascribed to the fact that, in the theory of the experimental method, the external friction ($\epsilon$) has been considered infinitely large in comparison with the internal friction or viscosity. Thus he introduced into the Kinetic Theory of Gases the slip coefficient $\zeta = \eta/\epsilon$, which Helmholtz [4] had previously defined for liquids.

## II. Determinations of the Coefficient of Slip in Air.

The first experimental determination of the value of the coefficient of slip was made by Kundt and Warburg [5] who used the capillary tube method. Their results were:

| Tube No. | Pressure. | Temperature. | $\zeta$. | $\zeta_{76} = \frac{\zeta \cdot p}{76}$. |
|---|---|---|---|---|
| 1..... | 33.8 mm | 15° C | .00017 | $76 \times 10^{-7}$ |
| 2..... | 39.0 " | 15° C | .00016 | $82 \times 10^{-7}$ |
| 2..... | 33.8 " | 15° C | .00018 | $80 \times 10^{-7}$ |
| | | | Mean..... | $79 \times 10^{-7}$ |

The mean of their values at 15° C and 76 cm is about $79 \times 10^{-7}$. Millikan in a preceding article has reduced this to 23° C, getting $\zeta_{76}$ at 23° C = $82 \times 10^{-7}$.

[1] Using Stokes' value $\sqrt{\eta/\rho} = .116$ for air, Maxwell made the first calculation of the mean free path of a gas molecule.

[2] Phil. Trans., 1866, Vol. 156, p. 249.

[3] Pogg. Ann., 1865, Vol. 125, p. 177.

[4] Wiener Sitzung., 1860, Vol. 40, p. 607.

[5] Pogg. Ann., 1876, Vol. 159, p. 399.

In the determination of the elementary electrical charge by the falling drop method Millikan [1] found that very small droplets of oil did not follow Stokes' equation

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho). \tag{2}$$

From his observations he made an empirical correction of the above equation, writing the corrected law in the form

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho)\left(1 + \frac{Al}{a}\right), \tag{3}$$

where $Al$ was determined from the curve of his observations. Millikan pointed out that the correction of Stokes' Law for Slip [2] gave

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho)\left(\frac{1 + 3\zeta/a}{1 + 2\zeta/a}\right), \tag{4}$$

which, for small values of $\zeta/a$, reduces to

$$v = \frac{2}{9}\frac{ga^2}{\eta}(\sigma - \rho)(1 + \zeta/a). \tag{5}$$

Thus, the $Al$ determined by Millikan was really the coefficient of slip for oil and air. His value for 23° C was $\zeta_{76} = 77 \times 10^{-7}$. In a later determination [3] a more detailed study of the failure of Stokes' Law for small oil drops gave the value $\zeta_{76}$ at 23° C $= 82.2 \times 10^{-7}$.

For small drops of shellac, Lee [4] observed $Al = \zeta_{76}$ at 76 cm and 23° C to be $100 \times 10^{-7}$.

These experimental results led Millikan to a theoretical study of slip for different boundary conditions. He concluded that when no gas molecules were regularly reflected after impact upon the walls, the maximum of external friction, and hence the minimum of slip, would result. For a mechanically rough surface, which would cause such diffuse reflection of all gas molecules, he calculated the minimum value of $\zeta$ at 23° C and 76 cm to be $65.9 \times 10^{-7}$.

## III. Theory for Slip Determinations by the Constant Deflection Method.

The theory of the Constant Deflection Method of determining viscosity coefficients gives

$$\eta = \frac{\pi I \phi}{\omega l T^2}\left(\frac{b^2 - a^2}{a^2 b^2}\right). \tag{6}$$

[1] Phys. Rev., 1911, 32, 382.
[2] Bassett, Hydrodynamics, Vol. II., p. 271.
[3] Phys. Rev., 1913, Vol. II., p. 139.
[4] Phys. Rev., 1914, IV., 420.

$I$ = moment of inertia of suspended cylinder; $\phi$ = angular displacement of suspended cylinder; $a$ = radius of suspended cylinder; $l$ = length of suspended cylinder; $T$ = period of oscillation of suspended cylinder; $\omega$ = angular velocity of outer cylinder; $b$ = radius of outer cylinder, when it is assumed that there is no slip at the surfaces of the cylinders. At ordinary pressures, this assumption involves an error too small to be observed by this method. For the case where slip becomes appreciable the complete equation as developed by Millikan is

$$\eta = \frac{\pi I \phi}{\omega l T^2}\left(\frac{b^2 - a^2}{a^2 b^2}\right)\left(1 + 2\zeta_p \frac{b^3 + a^3}{ab^3 - a^3 b}\right). \tag{7}$$

The slip term at atmospheric pressure may be calculated for this apparatus since $a = 5.3412$ cm, $b = 6.0632$ cm, and $\zeta_{76} = 66 \times 10^{-7}$ (from theory). This gives a value for the term

$$2\zeta_p \frac{b^3 + a^3}{ab^3 - a^3 b} = .00002$$

which is quite negligible, since the experimental error is about .1 per cent. Hereafter the equation (6) will be written

$$\eta_p' = \frac{\pi I \phi}{\omega l T^2}\left(\frac{b^2 - a^2}{a^2 b^2}\right) \tag{8}$$

and $\eta_p'$ defined as the apparent viscosity coefficient at the pressure $p$.

The value $\eta_{76}'$ will be taken as the true value of the viscosity coefficient. Equation (7) may now be written

$$\eta = \eta_p'\left(1 + 2\zeta_p \frac{b^3 + a^3}{ab^3 - a^3 b}\right) \tag{9}$$

and solving for $\zeta_p$

$$\zeta_p = \left(\frac{\eta}{\eta_p'} - 1\right)\frac{1}{k}; \qquad k = 2\left(\frac{b^3 + a^3}{ab^3 - a^3 b}\right). \tag{10}$$

Thus to determine the slip coefficient by this method it is necessary, first, to determine the coefficient of viscosity ($\eta = \eta_{76}'$) and then $\eta_p'$ at some other pressure. Application of equation (10) gives $\zeta_p$, and $\zeta_{76}$ is calculated from the formula $\zeta_{76} = \zeta_p(p/76)$. $\eta'$ and $\eta_p'$ must, of course, be observed at the same temperature or reduced to the same conditions by the proper formula.

The investigation of slip coefficients by this method was undertaken, at Prof. Millikan's suggestion, by E. L. Harrington [1] to determine whether the slip depended on the nature of the surface as the lack of

[1] PHYS. REV., 1916, VIII., p. 738.

agreement between the values for oil and shellac drops had indicated. Harrington devoted his time chiefly, however, to the improvement of the precision of the method of determining the viscosity coefficient, leaving the writer to carry on the slip determinations. The writer assisted Harrington for a short time in the first determinations of the slip coefficient. Some of Harrington's results will be included in this paper.

## IV. Adaptation of the Apparatus for Slip Determinations.

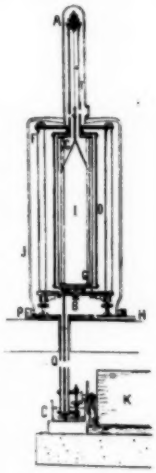

Fig. 1.

The Constant Deflection Apparatus consists essentially of two concentric brass cylinders, the inner, $I$, being suspended on an elastic suspension, $s$, so that, when the outer cylinder, $O$, is driven at a constant speed by a clock driving mechanism, $K$, a constant torque due to viscosity will cause a constant deflection of the suspended cylinder from its equilibrium position. To eliminate end effects the inner cylinder is suspended between two guard rings, $G$, of the same diameter and less than .3 mm from it. A small mirror mounted at the base of the suspension wire makes it possible to observe the deflection by a telescope and scale. The period of rotation ($t = 2\pi/\omega$) of the outer cylinder was determined by a chronograph attached to the driving mechanism.

The constants of the apparatus as determined by Harrington were used.

| | | |
|---|---|---|
| Moment of inertia of inner cylinder | $I$ = | 7617.3 |
| Radius of inner cylinder | $a$ = | 5.3410 cm |
| Length of inner cylinder | $l$ = | 24.88 cm |
| Radius of outer cylinder | $b$ = | 6.0632 cm |

For work at low pressures, the cylinders were set upon a steel plate, $P$, about 30 cm in diameter. A large-mouthed glass bottle, $J$, about 28 cm in diameter and 62 cm high was found and the mouth ground plane to fit tightly a rubber gasket laid on the steel base-plate. An opening was ground in the bottom of the bottle for the suspension head, $T$, which projected some 25 cm above the large bottle. A glass tube, $A$, sealed at the top was fitted by a ground glass joint into the bottom of the large bottle thus closing the apparatus. A plate glass observing window was sealed over a small hole in the side of the suspension cover to prevent distortion of the image seen in the observing mirror. A discharge tube for spectroscopic work was also sealed into the side of the suspension cover. The driving shaft for the rotating cylinder was led through an iron pipe,

$Q$, sealed into the steel base-plate. The lower end of this pipe was immersed in a vessel of mercury, $C$, thus sealing it from the outside. A rim around the edge of the base-plate made it possible to use a mercury seal at this joint and, the bottom of the bottle being somewhat concave, a mercury seal was also used at the upper joint. Thus the apparatus was enclosed tightly enough to permit evacuation to about .001 mm pressure.

A Gaede mercury pump backed by a rotary oil pump made it possible to reduce the pressure within the apparatus to .1 mm in a little over two hours. The volume of the apparatus was about 150 liters. Pressures were read by a McLeod gauge calibrated to read .0001 mm. Temperatures within the apparatus were read from a Beckmann thermometer which had been calibrated by comparison with a standard Baudin instrument. The observing telescope and scale were mounted about 200 cm distant from the suspended mirror and the deflection could be read to .1 mm. The steel suspension wire used throughout this work gave an observed scale deflection of 62 to 64 cm when the period of rotation of the outer cylinder was about 30 sec.

## V. Experimental Methods and Elimination of Errors.

The determination of the viscosity coefficient was made from the formula

$$\eta_p' = K \frac{t}{T^2} \tan^{-1} \frac{s}{2d} \qquad \text{where} \qquad t = \frac{2\pi}{\omega}; \qquad \phi = \tan^{-1} \frac{s}{2d},$$

$$K = I\left(\frac{b^2 - a^2}{2a^2b^2l}\right).$$

The period $T$ and the scale distance $d$ being determined beforehand, it was only necessary to observe $s$ and $t$ so that $\eta_p'$ could be calculated. Temperatures and pressures were read as already described.

Having determined $\eta_{76}'(=\eta)$, it was necessary to determine $\eta_p'$ at some low pressure and calculate $\zeta_{76}$ from the equations

$$\zeta_p = \left(\frac{\eta}{\eta_p'} - 1\right)\frac{1}{k} \qquad \text{and} \qquad \zeta_{76} = \frac{\zeta_p \cdot p}{76}.$$

For atmospheric pressure the observed scale deflection $s$ was about 63 cm with an error of .3 mm. At 0.12 mm pressure and $t = 30$ sec. the scale deflection was found to be about 56 cm. Thus a difference of 7 cm with an error of .3 mm in reading would give an apparent error of not more than 1 part in 200. The gauge reading to .0001 mm, this error should be only 1 part in 1,200. Errors in observing all the other factors were much less than these, so they may be neglected. It was found,

however, that the principal source of inaccuracy was due to change of the pressure during observations. This rise of pressure was considerable in the first few hours after evacuation was stopped, but reached a steady value after 24 hours or so. It was found by experiment that during the 10-minute interval necessary for one complete observation the pressure change was from .001 to .003 mm. After one or two days the pressure rose less than that in 24 hours. This was explained by supposing the increase in pressure to be due to gases released from the glass and metal surfaces. By taking pressure readings before and after each observation a fairly accurate mean value was obtained. The temperature was also read at frequent intervals and the mean value used. The apparatus being set up in a constant temperature room, the observations were made within a very narrow range (22° to 24° C). Variations from 23° C were corrected for by Millikan's formula (Ann. der Physik, 1913, Vol. 41, p. 759).

$$\eta_\theta = \eta_{23^\circ} - .000000493(23^\circ - \theta).$$

In the early work on slip determinations, a series of observations was made after a single evacuation. The values of $\zeta_{76}$ calculated from these observations gave an initial value of about $70 \times 10^{-7}$ but rose steadily until a value of $200 \times 10^{-7}$ was found about two weeks later. The pressure change was from .1238 to .1448 mm during this interval. Since $\zeta_{76}$ should be independent of the pressure, this indicates that the increase in pressure must be due to the presence of some gas of a lower viscosity than air. This suggested that hydrogen (viscosity about one half that of air) was being released from occlusion by the metal parts of the apparatus. Spectroscopic examination of the discharge tube showed a definite increase in the intensity of the hydrogen lines when the apparatus was allowed to stand several days at a low pressure.

Admission of air to full atmospheric pressure to flush out the apparatus and a second evacuation gave the same result, viz., a low value during the first two or three hours after the pumps were stopped, then a steady rise in the value of the slip constant $\zeta_{76}$. To eliminate this variation it was found advisable to admit air immediately after a set of observations was completed and to evacuate only a short time before readings were to be taken. Thus the time during which the "hydrogen effect" might be present was so short that it did not affect the results appreciably. It was found that the values of $\zeta_{76}$ obtained within three or four hours after an evacuation were quite consistent. Observations were usually made within an hour after evacuation. After many evacuations this "hydrogen effect" was less marked but was always present. By taking observations shortly after evacuation, it was avoided.

## VI. Table of Observations and Calculated Data for Brass Surfaces in Air.

*Results on Brass Surfaces in Air.*

$d = 200.5$ cm; $T = 175.48$; $\eta = 1822.6 \times 10^{-7}$.

| $S$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\eta_p \times 10^7$. | $\zeta_p \times 10^5$. | $p$ (mm). | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| 56.28.... | 30.134 | 23.04 | 1643.0 | 3884 | .1303 | 66.6 |
| 56.56.... | 30.040 | 23.05 | 1646.0 | 3811 | .1328 | 66.6 |
| 56.71.... | 30.034 | 22.76 | 1649.4 | 3701 | .1361 | 66.4 |
| 56.93.... | 29.989 | 22.81 | 1653.2 | 3616 | .1388 | 66.0 |
| 57.23.... | 29.500 | 22.67 | 1634.7 | 4044 | .1238 | 65.9 |
| 55.95.... | 30.267 | 22.67 | 1640.2 | 3912 | .1266 | 65.2 |
| 56.76.... | 29.992 | 22.72 | 1646.0 | 3726 | .1340 | 65.7 |
| 56.63.... | 30.124 | 22.72 | 1646.2 | 3721 | .1362 | 66.7 |
| 55.77.... | 30.187 | 22.81 | 1628.2 | 4166 | .1200 | 65.8 |
| 56.25.... | 29.975 | 22.82 | 1630.6 | 4107 | .1209 | 65.3 |
| 57.25.... | 29.720 | 23.70 | 1645.0 | 3856 | .1253 | 63.6 |
| 57.02.... | 29.880 | 23.66 | 1647.1 | 3797 | .1268 | 63.4 |
| 57.10.... | 29.795 | 22.81 | 1644.8 | 3764 | .1287 | 63.8 |
| 56.68.... | 30.032 | 22.81 | 1645.9 | 3738 | .1311 | 64.5 |
| 56.71.... | 30.134 | 22.80 | 1652.9 | 3570 | .1361 | 63.9 |
| 56.86.... | 30.079 | 22.83 | 1653.8 | 3556 | .1367 | 64.0 |
| 57.20.... | 29.929 | 22.82 | 1655.1 | 3520 | .1405 | 65.1 |
| 57.27.... | 29.922 | 22.79 | 1656.7 | 3480 | .1428 | 65.4 |
| 57.15.... | 30.000 | 22.80 | 1657.6 | 3459 | .1445 | 65.8 |
| 57.05.... | 30.053 | 22.73 | 1657.7 | 3451 | .1459 | 66.2 |
| 57.32.... | 29.922 | 22.79 | 1656.2 | 3437 | .1467 | 66.3 |
| 57.30.... | 29.930 | 22.77 | 1656.5 | 3444 | .1475 | 66.8 |
| 56.51.... | 29.952 | 22.87 | 1640.5 | 3836 | .1368 | 69.0 |
| 55.77.... | 29.917 | 22.84 | 1614.0 | 4469 | .1178 | 69.3 |
| 55.65.... | 30.000 | 22.78 | 1614.6 | 4436 | .1166 | 68.1 |
| 56.47.... | 29.873 | 22.90 | 1631.2 | 4053 | .1300 | 69.3 |
| 56.53.... | 30.037 | 22.42 | 1641.9 | 3733 | .1402 | 68.9 |
| 56.73.... | 30.043 | 23.01 | 1651.4 | 3405 | .1508 | 67.6 |
| 56.62.... | 29.915 | 22.73 | 1637.0 | 3886 | .1343 | 68.7 |
| 56.68.... | 30.102 | 22.84 | 1649.8 | 3591 | .1349 | 63.7 |
| 56.46.... | 30.100 | 22.81 | 1647.1 | 3646 | .1378 | 66.1 |
| 56.76.... | 30.018 | 22.79 | 1647.4 | 3630 | .1424 | 68.0 |
| 56.68.... | 29.972 | 22.87 | 1642.6 | 3762 | .1308 | 64.7 |
| 57.00.... | 29.860 | 22.99 | 1645.6 | 3710 | .1338 | 65.3 |
| 57.03.... | 30.158 | 23.33 | 1662.9 | 3338 | .1558 | 68.3 |
| 56.34.... | 30.080 | 23.46 | 1638.8 | 3915 | .1258 | 64.8 |
| Mean ... | | | | | | 66.15 |

The observations were made within a pressure range of .1 to .18 mm since at lower pressures the error due to change of pressure during an observation was large, while at pressures above .18 mm the deflection $s$ differed so little from the deflection at atmospheric pressure that the error of observing this difference became considerable.

In general, the experimental conditions were as follows:

Temperature — 22° C to 24° C
Pressure — .1000 mm to .1800 mm
Period ($t$) — 30 sec. ($\pm .2$)
Period ($T$) — 175.5 sec.

Scale deflection, for $p = 76$ cm − 630 mm
" $p =$ 0.18 mm − 580 mm } approximately
" $p =$ 0.10 mm − 550 mm

Observations were usually made in pairs within an hour after evacuation.

The mean value ($66.15 \times 10^{-7}$) is very close to Millikan's theoretical minimum value ($65.9 \times 10^{7}$) but is considerably lower than any of the values found by other methods for oil or for glass surfaces.

## VII. Determination of Slip for Shellac Surfaces in Air.

The cylinders were next coated with a thin layer of shellac, dried by an air blast and replaced in position. From the weight of the cylinders before and after the shellac was applied and the surface area of the cylinders, the average thickness of the shellac film was calculated. This was found to be .01 mm and made only a small correction in the values of the constants $a$ and $b$.

After the determination of the viscosity coefficient at atmospheric pressure, the pressure was reduced and observations made as before. At first a high value of $\zeta_{76} = 97 \times 10^{-7}$ was found while the shellac was fresh. Later, the values of $\zeta_{76}$ dropped steadily toward the minimum value. This result is shown in the two sets of data here given; the first set of observations being due to Harrington and the second to the writer. In two other trials, accidental experimental difficulties prevented the writer from making observations while the shellac was fresh but values between 80 and $90 \times 10^{-7}$ were found several days after application of the shellac. The fall in the observed value of the slip coefficient indicates a change in the surface due probably to oxidation of the shellac which seems to produce a rough surface.

*Data on Fresh Shellac Surfaces in Air.*

$d = 200.6$, $T = 176.00$.

*E. L. Harrington: Fresh Shellac, August 1, 1916.*

| Date. | $S$. | $t$. | $\theta$. | $\eta_p' \times 10^7$. | $\zeta_p \times 10^5$. | $p$ (mm). | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|---|
| Aug. 9..... | 55.93 | 29.719 | 23.38 | 1602.8 | 4911 | .1474 | 95.2 |
| | 55.72 | 29.727 | 23.44 | 1597.3 | 5059 | .1478 | 98.5 |
| Aug. 10, A.M.. | 53.42 | 29.715 | 23.76 | 1531.3 | 6842 | .1048 | 94.3 |
| | 52.55 | 29.960 | 23.86 | 1519.4 | 7188 | .1058 | 100.0 |
| Aug. 10, P.M.. | 53.99 | 29.936 | 23.67 | 1559.0 | 6080 | .1125 | 90.0 |
| | 53.19 | 30.263 | 23.60 | 1552.9 | 6240 | .1133 | 93.0 |
| Aug. 11, A.M.. | 53.43 | 30.227 | 23.46 | 1556.6 | 6121 | .1107 | 89.0 |
| | 52.96 | 30.440 | 23.50 | 1553.9 | 6204 | .1112 | 90.8 |
| Aug. 11, P.M.. | 55.19 | 30.100 | 23.13 | 1602.0 | 4886 | .1288 | 82.8 |
| | 55.14 | 30.100 | 23.13 | 1600.5 | 4920 | .1298 | 84.1 |
| Aug. 12..... | 56.94 | 29.827 | 23.64 | 1637.0 | 4099 | .1438 | 77.6 |
| | 56.75 | 29.917 | 23.70 | 1636.5 | 4108 | .1438 | 77.7 |
| Aug. 30..... | 57.28 | 29.780 | 23.10 | 1653.1 | 3538 | .1506 | 70.1 |

*L. J. Stacy: Fresh Shellac, March 7, 1917.*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Mar. 9, A.M.. | 56.04 | 29.789 | 23.36 | 1578.8 | 5588 | .1330 | 97.7 |
| | 55.92 | 30.010 | 23.40 | 1582.5 | 5381 | .1352 | 95.7 |
| Mar. 9, P.M.. | 57.66 | 29.800 | 23.14 | 1619.7 | 4580 | .1470 | 88.6 |
| | 57.26 | 30.080 | 23.19 | 1623.7 | 4486 | .1482 | 87.5 |
| Mar. 10, A.M.. | 58.15 | 29.723 | 23.55 | 1628.2 | 4414 | .1418 | 82.3 |
| | 57.76 | 29.983 | 23.59 | 1632.4 | 4318 | .1441 | 81.9 |
| Mar. 10, P.M.. | 57.56 | 30.164 | 23.53 | 1636.7 | 4206 | .1493 | 82.6 |
| | 58.12 | 29.896 | 23.50 | 1637.7 | 4179 | .1543 | 84.8 |
| | 57.30 | 30.322 | 23.24 | 1637.9 | 4152 | .1545 | 84.4 |
| Mar. 11..... | 56.83 | 29.985 | 22.87 | 1606.6 | 4876 | .1313 | 84.2 |
| | 56.06 | 30.432 | 22.86 | 1608.7 | 4820 | .1323 | 83.9 |
| Mar. 12..... | 57.38 | 30.334 | 23.12 | 1640.8 | 4066 | .1487 | 79.5 |
| | 57.77 | 30.188 | 23.21 | 1643.8 | 3999 | .1495 | 78.7 |
| Mar. 13..... | 57.75 | 30.144 | 23.52 | 1640.9 | 4102 | .1443 | 77.9 |
| | 58.05 | 30.031 | 23.52 | 1643.1 | 4048 | .1473 | 78.4 |
| Mar. 16..... | 58.16 | 30.169 | 23.07 | 1653.7 | 3747 | .1518 | 74.8 |
| Mar. 17..... | 57.42 | 30.084 | 22.85 | 1628.4 | 4242 | .1332 | 74.3 |

The following results were obtained using the same experimental method as with brass surfaces. The shellac surfaces were about two months old when the first readings were taken.

The results of these experiments furnish independent evidence of the fact that the viscosity of a gas is independent of the pressure, since $\zeta_{76}$ turns out to be a constant for a given surface in air. The value of $\zeta_{76}$ for rough surfaces checks Millikan's theoretically deduced values within the limit of error of the experiment. The variation in slip for different surfaces has been checked and the result for fresh shellac, $\zeta_{76} = 96.8 \times 10^{-7}$, is very close to the result Lee obtained, $\zeta_{76} = 100 \times 10^{-7}$, from the correction of Stokes' Law for falling shellac drops.

In conclusion the writer wishes to express his indebtedness to Professor R. A. Millikan who suggested the problem and directed the experimental

*Data for Old Shellac Surfaces in Air.*
$d$ = 200.6 cm; $T$ = 176.00 sec.

| $S$. | $t$. | $\theta$. | $\eta_p' \times 10^7$. | $\zeta_p \times 10^5$. | $p$ (mm). | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| 55.39.... | 30.027 | 23.67 | 1605.1 | 4833 | .1088 | 69.2 |
| 57.49.... | 29.767 | 24.28 | 1648.5 | 3875 | .1338 | 68.2 |
| 57.06.... | 30.076 | 24.34 | 1653.3 | 3767 | .1370 | 67.9 |
| 57.49.... | 30.023 | 23.11 | 1661.5 | 3443 | .1535 | 69.5 |
| 57.02.... | 30.058 | 22.76 | 1653.8 | 3639 | .1444 | 69.1 |
| 57.20.... | 30.123 | 22.87 | 1662.5 | 3431 | .1478 | 66.7 |
| 57.38.... | 30.023 | 22.90 | 1661.7 | 3447 | .1488 | 67.5 |
| 57.28.... | 30.074 | 22.95 | 1662.1 | 3444 | .1493 | 67.7 |
| 57.64.... | 29.885 | 22.92 | 1659.2 | 3507 | .1478 | 68.2 |
| 57.72.... | 29.930 | 22.97 | 1664.4 | 3392 | .1495 | 66.7 |
| 57.44.... | 30.144 | 23.08 | 1668.9 | 3299 | .1573 | 68.3 |
| 57.60.... | 30.050 | 23.11 | 1668.2 | 3317 | .1585 | 69.2 |
| 56.75.... | 30.111 | 23.24 | 1647.3 | 3830 | .1351 | 68.1 |
| 56.90.... | 30.112 | 23.28 | 1651.1 | 3744 | .1373 | 67.6 |
| 57.13.... | 30.067 | 23.21 | 1656.0 | 3613 | .1437 | 68.3 |
| 55.19.... | 30.014 | 23.06 | 1597.2 | 5032 | .1057 | 70.0 |
| 55.23.... | 30.087 | 23.10 | 1602.3 | 4910 | .1076 | 69.5 |
| 57.15.... | 30.210 | 23.57 | 1664.0 | 3464 | .1498 | 68.3 |
| 57.27.... | 30.271 | 23.66 | 1670.8 | 3316 | .1533 | 66.9 |
| 56.91.... | 30.211 | 23.21 | 1657.2 | 3585 | .1411 | 66.6 |
| 57.17.... | 30.174 | 23.31 | 1662.6 | 3469 | .1445 | 66.0 |
| 57.36.... | 29.963 | 22.55 | 1650.5 | 3823 | .1353 | 68.1 |
| 57.37.... | 30.019 | 22.58 | 1652.8 | 3793 | .1380 | 68.6 |
| 56.74.... | 30.300 | 22.51 | 1644.5 | 3780 | .1288 | 64.1 |
| 57.33.... | 30.161 | 22.87 | 1655.3 | 3742 | .1356 | 66.8 |
| 57.25.... | 30.160 | 22.86 | 1652.6 | 3806 | .1364 | 68.3 |
| 58.38.... | 29.508 | 21.94 | 1647.3 | 3835 | .1363 | 68.8 |
| 57.23.... | 30.152 | 22.12 | 1655.5 | 3777 | .1373 | 68.2 |
| Mean ... | | | | | | 67.7 |

This result is 2½ per cent higher than the value found for brass surfaces in air.

work; to the other members of the Physics Department of the University of Chicago for their interest and assistance throughout the investigation; and, in particular, to Dr. E. L. Harrington with whom the author worked in the first determination of slip by this method.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO,
September 22, 1922.[1]

[1] The work described in this paper was completed in February 1919.

# THE COEFFICIENTS OF VISCOSITY AND OF SLIP OF AIR AND OF CARBON DIOXIDE BY THE ROTATING CYLINDER METHOD.

By Karl Skillman Van Dyke.

Abstract.

**Coefficients of viscosity of air and of $CO_2$, determined by the constant deflection method.**—With the rotating cylinder apparatus designed by Millikan and used by Gilchrist, Harrington, Yen and Stacy in measurements of high precision, a new determination has been made of the coefficient of viscosity of dry air. The value obtained, $\eta_{23} = 1822.1 \times 10^{-7}$, is only 1/40 per cent less than the standard value of Harrington. The coefficient of viscosity of $CO_2$ obtained by the same method comes out $\eta_{23} = 1471.5 \times 10^{-7}$. The gas used was from c.p. $NaHCO_3$, and since, after purification by freezing, various samples gave concordant results, this value is thought to be correct to within 1/20 per cent. Comparison with the results of Breitenbach indicates that all his values, though relatively correct, are 1.5 per cent too high.

**Coefficients of slip for rough and smooth surfaces in air and $CO_2$** were computed from values of the apparent coefficients of viscosity measured by this method for pressures of 0.5 to 0.1 mm. For an *old shellac surface*, the values came out in both air and $CO_2$ only 3 per cent greater than the theoretical lower limit computed by Millikan for a completely diffusing rough surface, in agreement with Stacy's result; while for a surface *coated with watch oil*, the coefficients in air and $CO_2$ were respectively 21 and 12 per cent higher, in good agreement with the corresponding values found by Millikan's oil drop method. For clean and scratched *brass surfaces* intermediate values were obtained.

**Fatigue of a watch spring steel wire, twisted under load.**—In five years the period decreased 0.09 per cent, showing a gradual stiffening. A twist of 8° for half an hour caused a temporary zero shift of 0.004°.

## I. Introductory.

THE constant deflection method of studying the viscosities of gases, and, in particular, the rotating cylinder apparatus designed by Professor Millikan has heretofore yielded several determinations of viscosity coefficients for which a high degree of precision has been claimed: the viscosity of air determined by Gilchrist,[1] and redetermined by Harrington,[2] and the viscosities of oxygen, nitrogen and hydrogen by Yen.[3] It is one purpose of the experimental investigation herein described *to add the coefficient of viscosity of carbon dioxide to the above list of precisely known experimental magnitudes*. The main purpose, however, is to obtain

[1] Gilchrist, Phys. Rev., *1*, 124, 1913.
[2] E. L. Harrington, Phys. Rev., *8*, 738, 1916.
[3] K. L. Yen, Phil. Mag., *38*, 582, 1919.

further experimental evidence from the rotating cylinder method as to *how the external friction of a gas or the "coefficient of slip" depends upon the character of the bounding surface, and upon the nature of the gas in contact with it.* The results furnish convincing evidence for specular reflection of gas molecules against a bounding surface.

## II. The Rotating Cylinder Method.

In the rotating cylinder method the viscosity of a gas is obtained from the deflection of a suspended cylinder against a torsion fiber when a similar concentric cylinder is rotated at a constant speed. The deflection measures the viscous drag of one cylinder upon the other, and thus combines into a single measured effect both the internal friction of a layer of gas of known thickness and the external friction between the gas and the two bounding surfaces. The dimensions of the rotating cylinders in use are such that the viscous drag as measured by the deflection against the torsion fiber is sensibly independent of the pressure of the gas for pressures between atmospheric and ten centimeters of mercury. The falling off in deflection at ten centimeters of pressure is about one part in ten thousand (from the theory), at one to two centimeters pressure about 1 part in 1,000 (observable), at 1 or 2 millimeters of mercury about a per cent, while at pressures of one or two tenths of a millimeter the deflection is from ten to fifteen per cent less than its value at atmospheric pressure.

This falling off of the viscous drag through a gas at low pressures is interpreted by the kinetic theory not as any variation in the internal friction, but rather as resulting from a decrease in the friction at the bounding surface. Thus the kinetic theory holds $\eta$, the coefficient of viscosity, independent of pressure, and introduces from the hydrodynamical analog a coefficient of slip, $\zeta$, defined as the ratio of $\eta$ to the external friction.

The theory of viscosity and of slip determinations with the rotating cylinder apparatus has been given in a preceding paper by Professor Millikan. The working equations as used are given for convenience of reference. They are:

(1) $$\eta = k' l d,$$

(2) $$\eta = k' l d (1 + \zeta k),$$

(3) $$\zeta = \left( \frac{\eta_1}{\eta_2} - 1 \right) \frac{1}{k},$$

(4) $$k' = \frac{I(b^2 - a^2)}{4a^2 b^2 l D T^2},$$

$$k = 2 \left( \frac{b^3 + a^3}{ab^3 - a^3 b} \right),$$

where $\eta$ in (1) is the coefficient of viscosity, whether real (within the limits of error) as measured at a pressure of 10 cms of mercury or above, or apparent when measured at some pressure so low that the slip term in (2), the equation for the true value of the coefficient of viscosity, becomes significant. In these equations $k'$ is a constant of the apparatus in terms of the radii, $a$ and $b$, of the inner and outer cylinders, $I$ the moment of inertia of the suspended cylinder, $T$ the complete period of oscillation of the suspended cylinder in vacuo, $l$ the length of the inner cylinder, and $D$ the radial distance between the mirror mounted at the base of the suspension fiber and the curved scale upon which the deflection, $d$, is read when the outer cylinder is rotated steadily at the rate of one revolution every $t$ seconds.

The coefficient of slip, $\zeta_p$, is computed from two determinations of the apparent viscosity, one, $\eta_1$, at atmospheric pressure, and another, $\eta_2$, after evacuation to a pressure $p$ cms of mercury, by (3) above. This formula is obtained from (2) on the assumption that at the pressure at which $\eta_1$ is determined the second term can be neglected.

## III. The Apparatus.

The apparatus is that used by the previous observers referred to and its constants have been given by Harrington. The adaptation of the apparatus for working at low pressures is described by Stacy in a preceding paper. It suffices to repeat that the entire cylinder system is covered by a large glass jar (about 35 liters capacity) and the whole sealed with mercury. The rotating cylinder is driven mechanically through a mercury seal. A pressure as low as 0.001 mm is attainable. The only changes which have been made in the apparatus in the present work are in the deflection observing system and in the pumps used in evacuation.

A scale, distant about two and a half meters from the apparatus, curved to an arc, of which the suspension fiber was the center, was used for reading the deflections of the inner cylinder. The scale was illuminated from behind and the deflection observed against the cross hairs of a telescope mounted at a new observer's position in front of the chronograph (see diagram in Harrington's paper) and focused through two fixed auxiliary mirrors on the image of the scale in the deflecting mirror. No accuracy of the reading of deflection was sacrificed by the change in the observer's position, while much was gained in convenience of manipulation of the driving apparatus and chronograph, and in the convenience of temperature observation and control.

The scale used in the experimental work represented in the data of the first three tables was a flexible transparent celluloid scale divided

into millimeters and calibrated from time to time against a standard B. and S. steel meter scale. The celluloid scale was discarded later when its calibration showed a sudden change with the advent of damp summer conditions in a basement room. The standard B. and S. steel meter scale was then substituted for the celluloid scale, the steel rule being clamped onto a brass frame cut in an arc of radius 236 cms, and firmly mounted at approximately this distance from the suspension fiber. The transparent feature of the celluloid scale had been so convenient that a transparent glass scale (10 cms long and divided into mms) was mounted as a slider on the steel scale, and in all later work was moved back and forth from the zero position on the scale to the position of deflection. The deflection thus involved the sum of two differences, one on the steel scale (60 cm) and one on the glass rider (usually but a few millimeters). In practice it was found convenient to let the deflection swing about its mean position during the period of observation, the usual amplitude of the swings being but one or two millimeters, and the position of the cross hair was read at equal intervals (about 30 readings) and the mean of these used in computing the deflection.

It will be recalled that in Harrington's absolute determination of the viscosity of air much time was devoted to the study of suspension fibers, uncoiled stock for watch hair springs being finally adopted as most satisfactory, no zero shift being found. Harrington's "F" suspension (see his table of data) is still in use, but presents some shift of the zero with every deflection. This shift is very small, of the order of three tenths of a millimeter on the scale (at a distance of 236 cms from the mirror) under the normal deflection of about 70 cms for half an hour. The return of this zero to its original reading before the deflection requires from two to three hours. In all of the work to be reported a zero reading is taken by the method of small oscillations in common use in reading the position of the beam of an analytical balance before it comes to rest. The zero position is read in this way both before deflection and again as soon as possible (about three minutes) after the deflection is released, and the mean of these two used in computing the deflection. The whole error in reading the deflection cannot be greater than 0.3 mm when all of the factors are allowed for.

The pumps used in evacuating the apparatus between the high and low pressure viscosity determinations proved an important factor in the consistency of the results obtained for the coefficient of slip. For the determinations listed in Table III. the pumping system consisted of a large May-Nelson pump (oil) and a Gaede rotary mercury pump. The aim was to evacuate as rapidly as possible so that a determination of the

viscosity at the low pressure could be made before the effects of the release of occluded gases became serious, an effect which Stacy found troublesome. With this pumping system the total time of evacuation was more than two hours, and consistent results in slip coefficients were obtained only after some twenty or thirty attempts which were very inconsistent.

In all later slip work a mercury diffusion pump backed by the May-Nelson pump was used. This combination permitted a determination of the apparent viscosity at 0.1 mm to be made within an hour after that made at atmospheric pressure. No further trouble was had from varying values of slip on the surfaces listed following the installation of the diffusion pump.

## IV. Apparatus Constants and Experimental Conditions.

The constants of the cylinder, which should have shown no change since they were carefully determined by Gilchrist and again by Harrington, were not redetermined. They were taken from the latter's paper.

$a = 5.3412$ cm, $b = 6.0632$ cm, $l = 24.88$ cm, $I = 7{,}617.3$.

The period of the suspended system was determined from time to time in vacuo and the constancy of the suspension fiber watched in this way. It is interesting to note that the period of the suspended system is very closely the same as with previous observers, but that there is evidence of a gradual stiffening of the steel wire under continued strain. (In terms of the period, Harrington—175.58 seconds; Stacy—175.48; November, 1920—175.45; June, 1921—175.42 seconds.) This is but an instance of the known tendency of solids to harden when standing under strain.

The distance between mirror and scale was slightly increased over that used by previous observers, and was measured with a combination of meter sticks fastened together, and this in turn calibrated with the B. and S. steel meter.

$D$, 235.81 cms, when using celluloid scale,
$D$, 236.36 cms, when using steel scale.

Pressure readings were made on a McLeod gauge reading to 0.0001 mm. Errors in observing the pressure were considerably less than the rise in pressure over the interval required for a complete determination. This was usually two or three thousandths of a millimeter. Pressure readings were taken before and after each determination, and in many cases it was found possible to take several observations of pressure during the determination. The mean pressure was used in the computation of the coefficient of slip.

Temperatures were read every few minutes on a Beckman thermometer within the apparatus, and in most cases showed but two or three hundredths of a degree change during the fifteen minutes during which the observations were being taken. A high-grade thermometer hung beside the Beckman and its reading was also recorded at least once during the run. Both of these thermometers were calibrated against a standard Baudin Thermometer which had been calibrated at the Bureau International des Poids et Measures in Paris. In general the temperature was held fairly close to 23° C and the value of $\eta$ obtained corrected to 23° C by the linear formula

$$\eta_{23} = \eta_0 + k(23 - \theta),$$

where the coefficient for air is $4.93 \times 10^{-7}$ as used by Millikan,[1] and for $CO_2$ is $4.77 \times 10^{-7}$, this latter being computed by the substitution of Breitenbach's constants for $CO_2$ in the Sutherland equation.[2] For the small temperature differences involved the error introduced in the reduction is insignificant.

## V. Determination of the Viscosity of Air.

A complete absolute determination of the viscosity of dry air was made for the purpose of ascertaining how closely the value obtained by Harrington could be duplicated with the apparatus as set up. The apparatus was not dismantled, but left as found. Harrington's values of the dimensions of the cylinders were used but the period of the suspended system was redetermined. Table I. gives the observed data and the computed viscosities. It is not the intention to present an absolute determination, but rather to illustrate the type of consistency to be expected in repeating determinations with the apparatus. Also the mean $\eta_{23}$ of Table I. is taken as a calibration of the apparatus and to be used in making relative to Harrington's value for air the determination of the viscosity of carbon dioxide next described.

Table I.

*Viscosity of Dry Air.*

$T = 175.45$ sec., $D = 235.81$ cm, $k' = 8.2789 \times 10^{-7}$.

| $d$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\eta_0 \times 10^7$. | $\eta_{23} \times 10^7$. |
|---|---|---|---|---|
| 71.12..... | 30.951 | 23.13 | 1822.3 | 1821.7 |
| 71.44..... | 30.805 | 23.12 | 1821.9 | 1821.3 |
| 71.36..... | 30.865 | 23.24 | 1823.5 | 1822.3 |
| 71.42..... | 30.858 | 23.27 | 1824.6 | 1823.3 |
| 71.27..... | 30.904 | 23.27 | 1823.4 | 1822.1 |

Mean $\eta_{23} = 0.00018221$.
Harrington's Mean $\eta_{23} = 0.00018226$.

[1] R. A. Millikan, Ann. der Phys., *41*, 759, 1913.
[2] P. Breitenbach, Ann. der Phys., *5*, 166, 1901.

## VI. Determination of Viscosity of Carbon Dioxide.

Carbon dioxide was prepared by heating $NaHCO_3$ in a closed glass system. The gas formed was passed through two tubes containing $P_2O_5$ and collected in a five-liter jar, from which it was removed from time to time during the preparation and frozen under liquid air for storage in quantity. Several different lots of carbon dioxide were made in this way, and from two different samples of the carbonate. One was Merck's "Highest Purity," and the other, Baker's "Analyzed." The carbon dioxide as stored under liquid air was exposed to the Gaede pump for a considerable time, and then as the pumping continued the liquid air was replaced by a thick paste of alcohol at a temperature of about − 120° C. The carbon dioxide gradually evaporated from this as the alcohol rose in temperature, and was allowed to enter the apparatus after the first two or three samples were pumped off. The last portions of the solid carbon dioxide were always discarded.

The viscosity determinations are listed in Table II. They were made

Table II.

*Viscosity of $CO_2$.*

$T = 175.42$ secs., $D = 235.81$ cms, $K' = 8.2815 \times 10^{-7}$.

| $d$ (cm). | $l$ (cm). | $p$ (cm). | $\theta$ (° C). | $\eta_\theta \times 10^7$. | $\eta_{23,p}$. | $\eta_{23}$. |
|---|---|---|---|---|---|---|
| 57.48.... | 30.918 | 67 | 22.97 | 1471.7 | 1471.8 | 1471.8 |
| 57.44.... | 30.931 | 67 | 23.03 | 1471.3 | 1471.2 | 1471.2 |
| 57.47.... | 30.918 | 35 | 23.16 | 1471.7 | 1470.9 | 1470.9 |
| 57.66.... | 30.816 | 35 | 23.22 | 1471.7 | 1470.7 | 1470.7 |
| 57.52.... | 30.845 | 10 | 22.88 | 1469.4 | 1470.0 | 1470.2 |
| 57.50.... | 30.886 | 10 | 23.01 | 1470.9 | 1470.9 | 1471.1 |
| 57.77.... | 30.746 | 6 | 22.95 | 1471.1 | 1471.3 | 1471.6 |
| 57.70.... | 30.760 | 2.1 | 23.03 | 1470.0 | 1469.9 | 1470.7 |
| 57.68.... | 30.772 | 2.1 | 23.07 | 1470.1 | 1469.8 | 1470.4 |
| 57.77.... | 30.772 | 2.5 | 23.16 | 1472.3 | 1471.5 | 1471.9 |
| 57.73 ... | 30.793 | 2.5 | 23.21 | 1472.3 | 1471.3 | 1471.7 |

Mean $\eta_{23} = 1471.1$.

Mean $\eta_{23}(CO_2)$ relative to Harrington's $\eta_{23}(\text{air}) = 1471.5$.

upon four different samples of the gas. The last of these samples was subdivided for the different determinations listed into three fractions after the first determination of its viscosity as a whole was made. This division was made in the following way in an attempt to obtain some indication of the homogeneity of the sample. A liquid-air trap was opened to the apparatus after the determination was made, and carbon dioxide slowly drawn back to the trap and there solidified. As the

pressure fell the first trap was closed off and a second one exposed, this taking the second portion of the gas. The viscosity of the last third was then determined, and in succession the other two. Their viscosity determinations are all in agreement to within the limits of error in these determinations. It will be noted that in this table a number of the determinations were made at pressures ($p$) far below atmospheric. The individual values determined, $\eta_p$, are corrected to the true viscosity, $\eta$, in the last column by the addition of a small slip correction easily approximated from the slip determinations to be described.

When the mean for the values for $CO_2$ is made relative to Harrington's $\eta_{23}$ for air by correction in the proper ratio, $\eta_{23}$ for $CO_2$ becomes $1{,}471.5 \times 10^{-7}$. Relative to air this is probably correct to a part in several thousand.

Determinations of the viscosity of $CO_2$ by other methods have given rather varying values. Lassalle [1] and Ishida [2] have obtained values $1{,}490 \times 10^{-7}$ and $1{,}471 \times 10^{-7}$ respectively, both from oil drop experiments and both relative to the same $\eta_{23}$ for air, namely $1{,}823 \times 10^{-7}$. Ishida's value is in excellent agreement with the present determination. As pointed out by Lassalle, Breitenbach's value obtained from the capillary method when corrected to 23° C by the Sutherland formula and made relative to Harrington's value for air in the same ratio as his own value for air is higher than Harrington's becomes $1{,}474 \times 10^{-7}$. It is felt, however, that the precision obtained from the constant deflection method is of a different order entirely from that given by the other methods, and that the value given is probably correct to at least one part in 2,000. It speaks well for the correctness of the *relative* values of viscosities usually quoted, viz., those of Breitenbach,[3] that there is but 0.2 per cent of difference between the absolute value for $CO_2$ of $\eta_{23}$ as found herewith, viz., $1{,}471.5 \times 10^{-7}$, and the value computed by multiplying Harrington's value for air by Breitenbach's ratio of $\eta_{23}$ (air) and $\eta_{23}$ ($CO_2$). All of Breitenbach's absolute values, however, must be considered as 1.5 per cent too high.

As a further check on the accuracy of the relative value obtained in the foregoing work the apparatus was twice dismantled and reassembled without, however, any change in the suspension. The relative deflections due to the successive insertion into the apparatus of air and $CO_2$ give, in terms of Harrington's value for air, $1{,}471.9 \times 10^{-7}$ and $1{,}472.2 \times 10^{-7}$ as against $1{,}471.5 \times 10^{-7}$ reported above.

[1] L. J. Lassalle, PHYS. REV., *17*, 354, 1921.
[2] Y. I. Ishida, PHYS. REV., April, 1923.
[3] P. Breitenbach, Wied. Ann., *67*, 803, 1899.

## VII. Slip Determinations.

The experimental procedure in the determination of the coefficient of slip was much the same as that described by Stacy.[1] A viscosity run was first made upon the gas in the apparatus either at atmospheric pressure or at some pressure equivalent to it for viscosity determinations. In order to avoid the temperature disturbances which occurred within the apparatus when it was rapidly evacuated from atmospheric pressure the viscosity determinations were often made at a pressure of from 2 to 10 cms, and the slight slip correction involved in the viscosity at these pressures added. The apparatus was then evacuated as rapidly as possible to some pressure in the range of 0.1 mm to 0.4 mm and as soon as pressure conditions had become steady a second run was taken.

### Table III.

*Slip with Old Shellac Surfaces.*

$\eta_{22_{air}} = 1822.1$, $T = 175.42$ sec., $D = 235.81$ cms,
$\eta_{22_{CO_2}} = 1471.1$, $K' = 8.2815 \times 10^{-7}$, $k = 2.815$.

*Air.*

| $p$ (mm). | $d$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\eta_p \times 10^{-7}$. | $\zeta_p$. | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| .173..... | 65.43 | 30.945 | 23.05 | 1675.8 | .0309 | 70.0 |
| .250..... | 67.25 | 30.881 | 23.02 | 1718.7 | .0212 | 69.5 |
| .397..... | 68.81 | 30.888 | 23.46 | 1759.2 | .01295 | 67.7 |
| .425..... | 68.95 | 30.906 | 23.11 | 1763.8 | .01160 | 65.0 |

Mean $\zeta_{76}$ (air) $= 68.0 \times 10^{-7}$.
Millikan's theoretical value for a rough surface $= 65.9 \times 10^{-7}$.
Difference, + 3 per cent.

*$CO_2$*

| | | | | | | |
|---|---|---|---|---|---|---|
| .460..... | 56.42 | 30.832 | 22.71 | 1440.5 | .0715 | 43.2 |
| .459..... | 56.59 | 30.739 | 23.07 | 1440.5 | .0753 | 45.4 |
| .260..... | 55.60 | 30.774 | 23.04 | 1416.9 | .137 | 46.8 |
| .250..... | 55.69 | 30.789 | 23.04 | 1419.9 | .129 | 42.5 |
| .228..... | 55.46 | 30.775 | 23.03 | 1413.4 | .1425 | 42.8 |
| .183..... | 54.80 | 30.802 | 22.95 | 1397.8 | .1860 | 44.8 |
| .176..... | 54.82 | 30.791 | 23.20 | 1397.8 | .1880 | 43.5 |
| .146..... | 54.04 | 30.822 | 23.30 | 1379.4 | .241 | 46.3 |
| .142..... | 54.16 | 30.782 | 23.19 | 1380.6 | .236 | 44.2 |
| .135..... | 53.74 | 30.795 | 23.01 | 1370.5 | .2605 | 46.5 |
| .130..... | 53.75 | 30.775 | 23.00 | 1369.9 | .2618 | 44.7 |
| .103..... | 52.70 | 30.943 | 23.06 | 1350.5 | .318 | 43.0 |
| .095..... | 52.18 | 30.854 | 23.03 | 1333.3 | .3665 | 45.7 |

Mean $\zeta_{76}$ ($CO_2$) $= 44.57 \times 10^{-7}$.
Millikan's theoretical value for a rough surface $= 43.2 \times 10^{-7}$.
Difference, + 3 per cent.

[1] Stacy, preceding paper.

In the data given in Table III. the practice was to take two or three runs following each evacuation. Only the first of these is given in the table on air as the rise in the coefficient which occurred on standing at the low pressure was so rapid as to seriously distort the consistency obtained by taking the run as soon as possible after the evacuation. This rise was of the order of 3 per cent an hour in the coefficient of slip, and is attributed as in Stacy's work to the release of occluded gases of lower viscosity from the walls of the vessel and apparatus. A definite rise in pressure at the rate of about 0.001 mm per hour after the first hour was also noticeable.

In the case of the determinations made on carbon dioxide, less trouble was experienced from this effect, and in the data listed in the table the two determinations made after evacuation are listed.

In slip work done with the apparatus before the present investigation was started, the brass surfaces had been treated with a thin coat of shellac. The data in Table III. are for this old shellac surface.

## VIII. Slip Determinations on Different Surfaces.

### *Clean Brass.*

The apparatus was completely dismantled and the cylinders washed with alcohol and ether, until the brass surfaces appeared fairly bright

TABLE IV.

*Slip with Brass Surfaces—Air Only.*

$k = 2.815$.

| $p$ (mm). | $d$ (cm). | $d'$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\zeta_p$. | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| .519..... | 69.484 | 71.73 | 30.800 | 22.53 | .1147 | 78.3 |
| .511..... | 69.531 | 71.82 | 30.745 | 22.34 | .1168 | 78.6 |
| .356..... | 68.519 | 71.675 | 30.834 | 22.73 | .1638 | 76.6 |
| .232..... | 66.446 | 71.545 | 30.918 | 22.94 | .2405 | 73.6 |
| .175..... | 65.859 | 71.91 | 30.830 | 23.81 | .326 | 75.0 |
| .1743.... | 65.35 | 71.49 | 30.95 | 22.95 | .334 | 76.6 |
| .163..... | 64.994 | 71.46 | 30.955 | 22.70 | .354 | 75.8 |
| .109..... | 62.548 | 71.81 | 30.864 | 22.31 | .527 | 75.6 |
| .105..... | 62.394 | 72.10 | 30.804 | 23.24 | .543 | 74.9 |
| .0915.... | 61.194 | 71.93 | 30.774 | 22.99 | .623 | 74.9 |
| .086..... | 60.896 | 71.98 | 30.746 | 22.93 | .647 | 73.2 |
| .0813.... | 60.614 | 72.01 | 30.724 | 22.78 | .678 | 71.4 |

Mean $\zeta_{76}$ (air) $= 75.4 \times 10^{-7}$.

and clean. The coefficient of slip for this clean brass surface was then determined as before. (See Table IV., air only.) The new pumping system and the steel scale described above were used during this and later slip work, and the occluded gas effect was very little noticed in the values obtained for $\zeta_{76}$. In the tables for this later slip work, Tables IV. to VI., the column $d'$ gives the deflection obtained in cms for the gas in the apparatus taken at the equivalent of atmospheric pressure for viscosity immediately before evacuating and reduced to the temperature of the slip run and to the same driving speed as the slip run. The difference in the deflections, which is the measure of slip, is thus evident in each case.

*Watch Oil.*

The cylinders were then coated with watch oil such as is used in Millikan's oil drop experiments. The oil was applied with a camel's

TABLE V.

*Slip with Oil Surfaces.*
$k = 2.807$.
*Air.*

| $p$ (mm). | $d$ (cm). | $d'$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\zeta_p$. | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| .574..... | 69.816 | 72.02 | 30.742 | 22.80 | .1131 | 84.4 |
| .290..... | 67.729 | 72.00 | 30.693 | 22.27 | .226 | 85.1 |
| .163..... | 65.001 | 71.98 | 30.717 | 23.44 | .3877 | 81.5 |
| .157..... | 64.889 | 72.14 | 30.710 | 22.97 | .3975 | 81.1 |
| .129..... | 63.344 | 71.99 | 30.752 | 22.70 | .490 | 82.1 |
| .1258.... | 63.409 | 72.18 | 30.724 | 22.94 | .492 | 80.2 |
| .118..... | 62.860 | 72.10 | 30.720 | 22.87 | .528 | 80.9 |
| .107..... | 61.995 | 71.95 | 30.738 | 22.59 | .577 | 80.0 |
| .075..... | 58.747 | 72.00 | 30.729 | 22.72 | .809 | 78.8 |

Mean $\zeta_{76} = 81.8 \times 10^{-7}$,
Millikan's value from oil drop data $= 81.36 \times 10^{-7}$.

*$CO_2$.*

| | | | | | | |
|---|---|---|---|---|---|---|
| .2219.... | 55.505 | 58.20 | 30.739 | 22.91 | .1722 | 50.2 |
| .2015.... | 55.269 | 58.24 | 30.694 | 22.66 | .1917 | 50.6 |
| .1068.... | 53.015 | 58.25 | 30.716 | 22.98 | .352 | 49.5 |
| .0936.... | 52.328 | 58.26 | 30.705 | 22.78 | .403 | 49.6 |

Mean $\zeta_{76} = 50.0 \times 10^{-7}$.
Lassalle's value from oil drop data $= 50.7 \times 10^{-7}$.

hair brush in as thick a coat as would hold to a vertical surface and then allowed to run down the vertical cylindrical surfaces over night. Drops collecting at the bottom were then removed and the apparatus assembled. In assembling the outer cylinder was not allowed to come into contact with the inner one in any way for fear of causing some of the oil to bridge the gap between the inner suspended cylinder and its guard rings. During the course of the four following days the determinations of slip given in Table V. were made. During this time there was no indication of any oil bridging the gap in question. This would have been immediately evident in the period of oscillation of the suspended cylinder and in the consistency with which the inner cylinder took up its zero position or its deflection position after displacement. These indications were very carefully watched for and no case of suspected sticking was found.

*Scratched Brass.*

The watch oil was then removed with benzine and the cylinders carefully washed with alcohol and ether, and an attempt made to roughen the surfaces with a medium grain emery paper (Barton No. 2). Upon this roughened brass surface the determinations of slip listed in Table VI. were made.

TABLE VI.

*Slip with Scratched Brass.*

$k = 2.815$.

*Air.*

| $p$ (mm). | $d$ (cm). | $d'$ (cm). | $t$ (sec.). | $\theta$ (° C). | $\zeta_p$. | $\zeta_{76} \times 10^7$. |
|---|---|---|---|---|---|---|
| .394..... | 68.884 | 71.66 | 30.744 | 22.15 | .143 | 74.0 |
| .321..... | 69.053 | 72.41 | 30.735 | 22.67 | .173 | 73.0 |
| .2822.... | 68.087 | 71.95 | 30.749 | 22.51 | .2015 | 74.7 |
| .277..... | 67.902 | 71.67 | 30.757 | 22.31 | .195 | 71.8 |
| .141..... | 64.514 | 71.45 | 30.855 | 22.36 | .382 | 70.9 |
| .135..... | 63.254 | 71.91 | 30.722 | 22.51 | .485 | 72.5 |

Mean $\zeta_{76}$ (air) $= 72.8 \times 10^{-7}$.

*$CO_2$.*

| | | | | | | |
|---|---|---|---|---|---|---|
| .359..... | 56.561 | 57.91 | 30.762 | 22.40 | .0845 | 40.0 |
| .316..... | 56.241 | 57.91 | 30.758 | 22.43 | .105 | 43.7 |
| .107..... | 53.424 | 57.93 | 30.742 | 22.42 | .300 | 42.2 |
| .0895.... | 52.678 | 57.88 | 30.780 | 22.43 | .350 | 41.3 |

Mean $\zeta_{76}$ ($CO_2$) $= 41.8 \times 10^{-7}$.

In the slip constant of the instrument,

$$k = 2\frac{b^3 + a^3}{ab^3 - a^3b},$$

the thickness of the oil layer on the cylinders must be allowed for as changing the effective radii of the cylinders. It is evident from the formula that the oil layers are effective through the factor $(b - a)$ in the denominator to the extent that each added surface layer 0.01 mm thick increases $k$ by about 3 parts in 2,000. It is also evident that the viscosity constant of the apparatus

$$K = \frac{b^2 - a^2}{a^2b^2l}$$

is decreased in the same ratio. From this latter effect on the viscosity (using air) an estimate of the probable thickness of the oil layer was obtained. A change of three tenths of a per cent was found as due to the oil layer, which is about the effect that would result from a coat of oil on each surface 0.01 mm thick. In the results given in the table on oil surfaces this change has been allowed for.

## IX. Discussion of Results.

The error involved in any single determination of the coefficient of slip is that of determining a difference between two apparent viscosities, and as such is dependent on the accuracy with which each of the two viscosity determinations can be made. The agreement shown in Tables I. and II. is evidence that even where the gas content of the apparatus is changed between determinations and the individual values involve temperature, angular speed of rotation and deflection, the individual values differ less than one part in two thousand from a mean. On the basis of this maximum error in both of the viscosity determinations used to compute a single value of slip, this value may be in error as much as 3.0 per cent if the slip run is in air at 0.4 mm pressure, 1.5 per cent if at 0.25 mm pressure, and 1.0 per cent if at 0.15 mm pressure. For carbon dioxide the errors possible at these pressures are twice those for air. The values of the coefficient of slip obtained show an agreement among themselves well within this allowance. It is noticeable in the tables that at the higher pressures the values computed are considerably further from a mean than at the lower.

On the above consideration it might seem justifiable to weight each individual value according to the size of the difference from which it was obtained. This discrimination in favor of the lower pressures is thought

not altogether justified, for the idea of this coefficient of slip is, as taken over from hydrodynamics, merely a first approximation valid only as the decreasing external friction begins to be a factor. It is also to be noted that for a pressure of 0.1 mm the distance between the two cylindrical surfaces amounts to but ten mean free paths of air, and that when carbon dioxide is used, ten mean free paths correspond to a pressure of about 0.07 mm.

The justification of the reduction of the coefficient of slip to the coefficient at atmospheric pressure lies in the individual values of $\zeta_{76}$ thus obtained being independent of the pressure from which they were obtained. Upon the consideration of the errors incident to the determinations at the higher pressures used, which have just been given, it will be seen that the range of values of $\zeta_{76}$ obtained in any one of the tables does not constitute evidence of the dependence of $\zeta_{76}$ on pressure. In Table III. the values of $\zeta_{76}$ are least as obtained from higher pressures, the widest departures coming at the highest pressures where the errors must be greatest. The direction of these departures is seen to be the reverse in this table from that found in Table V., for example. In general, however, it will be seen that the higher pressures are not consistent in indicating any particular direction of departure from the mean value of $\zeta_{76}$, and the departures all fall within the limits of the errors expected at the particular pressure used. For pressures below 0.1 mm this is not true, for there seems to be a tendency of the values of $\zeta_{76}$ to fall off as the pressures are made lower than about this value. In view of the possible changes in the character of the gas at the extremely low pressures and the fact that the distance between the cylinders and the mean free path become comparable at the lower pressures, it has been somewhat arbitrarily decided to draw the lower limit of the region from which the value of the coefficient of slip is here obtained at about 0.1 mm for air and about 0.08 mm for $CO_2$. Accordingly the means of the values of slip obtained in this region are listed together in Table VII. and presented as the values of the coefficients of slip of air and of carbon dioxide for the surfaces used.

The results shown in Table VI. may seem at first somewhat inconsistent since the mean value of $\zeta_{CO_2}$ for the scratched brass is there given as $41.8 \times 10^{-7}$ while the lower theoretical limit is $43.2 \times 10^{-7}$. However, as indicated above, the experimental error with $CO_2$ is such that both the value found for the old-shellac surface, viz., $44.6 \times 10^{-7}$, and that for the scratched brass are, within that error, identical with that corresponding to a rough body, viz., $43.2 \times 10^{-7}$. That the same scratched surface was not quite rough with respect to *air* shows again the dependence of the character of the reflection upon *the nature of the gas*.

The definite variation of external friction with the character of the surface shows with great conclusiveness that the law which governs the return of gas molecules from the surface against which they strike must be different for different surfaces. If diffuse reflection were a general phenomenon there would be no possibility of a variation of $\zeta$ with the character of the surface. There must then be some relation between the direction of the molecules to and away from the surface. Maxwell explained the possible differences in external friction of a gas as due to the diffuse reflection of a part of the molecules from the walls of the containing vessel, and to the specular reflection of the remainder, the coefficient of slip taking higher values as the fraction reflected specularly is greater. From this it would be concluded that the oil surface presents a "smoother" surface to both air and carbon dioxide than does either of the other surfaces used. Furthermore, from a computation of the factor $(2 - f)/f$ which appears in the formula for the external friction following Maxwell (where $f$ is the per cent of total incident molecules reflected diffusely) using only the ratios of the slip coefficients listed in Table VII., the watch oil surface is seen to be from four to seven per cent more specular to air than to carbon dioxide, the scratched brass surface from eight to fifteen per cent more, and the old-shellac surface about equally specular to the two gases.

## X. Comparison with the Slip Results of Other Observers.

As shown in the tables, from his oil drop experiments Millikan [1] has obtained for the value of $\zeta_{76}$ for this same oil and air $81.4 \times 10^{-7}$, in place of my value 81.8, while Lassalle's [2] work with the oil and $CO_2$ yielded $50.7 \times 10^{-7}$ in place of my 50.0. Both of these are then in remarkable agreement with the present values. Also Ishida [3] obtained for oil and air $81.2 \times 10^{-7}$ also in close agreement, but for the $CO_2$ and oil, his value, namely $52.3 \times 10^{-7}$, is slightly higher than mine. These comparisons are

Table VII.

Mean $\zeta_{76} \times 10^{7}$.

| | Air. | $CO_2$. |
|---|---|---|
| Theoretical lower limit | 65.9 | 43.2 |
| Old shellac | 68.0 | 44.6 |
| Clean brass | 75.4 | |
| Scratched brass | 72.8 | 41.8 |
| Watch oil | 81.8 | 50.0 |

[1] Millikan, Phys. Rev., 2, 139, 1913.

[2] Lassalle, loc. cit.

[3] Ishida, loc. cit.

made with the oil drop work by reducing the constant "A" in that work to $\zeta_{76}$ by multiplication by the value of $l$ as computed from the equation $\eta = 0.3502nm\bar{c}l$. The same general discrimination of the oil surface between the molecules of air and carbon dioxide is seen in the above values from the oil drop as from the present work.

In conclusion the author wishes to acknowledge his indebtedness to the staff of Ryerson Laboratory, and in particular to Professor Millikan under whose direction the problem was undertaken, for constant and helpful interest and advice during the progress of the work.

RYERSON PHYSICAL LABORATORY,
CHICAGO UNIVERSITY,
September 22, 1922.[1]

[1] The work described above was completed in August, 1921.

# THEORY OF THE ELECTRIC ARC.

By K. T. Compton.

Abstract.

**Theory of the electric arc.**—(1) *Thermionic emission from the cathode.* The fundamental phenomena of the arc are the cathode fall and the copious emission of electrons from the cathode. J. J. Thomson first suggested that this emission is chiefly of thermionic origin. But is thermionic emission sufficient to account for observed primary arc currents? Using the best data as to the emission from carbon and tungsten, the computed thermionic currents in the case of the carbon arc, the tungsten arc in hydrogen, and low-voltage, low-pressure arcs in various gases are found to be of the right order of magnitude. Bräuer attempted to measure the thermionic emission directly by suddenly reducing the arc voltage to below the ionizing potential and obtained low values; but from a discussion of the effect of space charge on the current from the cathode it is shown that he certainly did not measure the thermionic emission but probably measured only the fraction released as a result of the effect on the space charge of positive thermionic emission from the anode. These facts and others all favor the thermionic theory as against the photo-electric and canal-ray theories of the origin of the electronic emission. (2) *Current carried by positive ions, and cathode fall.* If $i$ is the current density of electronic emission, there must be a current density of positive ions $j = i/242M^{1/2}$ to neutralize the space charge due to $i$, where $M$ is the atomic weight of the ions, and also an additional positive current density $J$ to maintain the excess positive space charge. From theoretical considerations it is found that $J = 1.47(10)^{-7} V_c^{3/2}\lambda^{1/2}/M^{1/2}c^{5/2}$, where $V_c$ is the cathode fall in volts, $\lambda$ the electronic mean free path, and $c$ is the cathode dark space. Incidentally, since $c$ is approximately equal to $\lambda$, $J$ varies as the square of the pressure. An application of this expression to several cases, the carbon, hydrogen, and mercury arcs, leads to reasonable values for $J$. The ratio of positive to negative currents, $(j + J)/i$, is computed also from energy considerations at the cathode for various cases, with results that are consistent with the values obtained independently from the above equations. This is good evidence for the general correctness of the theory. (3) *Ionization in the region between the electrodes* of a carbon arc must be sufficient to neutralize the space charge due to the electrons. Reasons are given for concluding that neither emission from the anode nor ionization by collision will account for this ionization but that it is primarily of thermal origin. An expression for the current is derived and it is found that if the temperature is 4000° K or over, and if the ionizing potential is about 8.6 volts or less, the thermal ionization estimated by applying Nernst's Heat Theorem, alone is sufficient. Photo-electric ionization if present would be secondary, a result of the radiation accompanying recombination. (4) *The anode fall* is accounted for in a qualitative way by a deficiency of positive ions near the anode due to decreased recombination. Thermionic emission from the anode may also play a part.

**Limitation of electronic current from a hot cathode by space charge.**—The equation for the case of elastic impacts: $i_e = 5.24(10)^{-6}(V^{3/2}/d^2)(\lambda/d)$ amp./cm², becomes $i_i = 5.45(10)^{-6}(V^{3/2}/d^2)(\lambda/d)^{1/2}$ amp./cm², for inelastic impacts.

THE complexity of the phenomena occurring in the ordinary electric arc has caused a wide divergence of opinion as to which phenomena are fundamental to its operation. Child [1] has given an excellent summary of experimental investigations and theories prior to 1913, and a number of papers have been published within the past few years. The data at our disposal include values of the cathode drop of potential, the anode drop, the electric intensity in the arc, the influence of the size and material of the electrodes, the nature and pressure of the surrounding gas, the current, the temperature of the electrodes, the rate of consumption of the electrodes, the spectrum and the intrinsic brightness of the arc, the mechanical reaction and the back electromotive force at the electrodes. The conclusions regarding the fundamental explanation of the arc have been conflicting.

In 1890 Fleming [2] suggested that the arc is due to a stream of negatively charged carbon atoms from the cathode, and experiments on the consumption of carbon in the electric arc led Duffield [3] to the same view.

Sir J. J. Thomson [4] suggested that the current from the arc is chiefly of thermionic origin, consisting of the electronic emission from the cathode plus a relatively small current arising from ionization of the gas by these electrons. This ionization is essential because positive ions are necessary in sufficient number to create a positive space charge around the cathode, thus permitting the escape of the electrons from it. All physicists now concur in the view that electronic emission from the cathode is of primary importance in the arc. This view has recently received strong additional support in the interesting work of Duffield, Burnham and Davis,[5] who showed that the mechanical reaction on the cathode in an arc was of the magnitude to be expected if due to the thermionic emission of electrons, but was much too small to be attributed to the expulsion of particles with values of $e/m$ of atomic size. But J. J. Thomson's view that these electrons are of *thermionic* origin has not been universally accepted.

Child [6] calls attention to the fact that the observed current density at the hot spot of the cathode is of the order of 318 amperes per sq cm, whereas Richardson's measurements of thermionic emission from carbon,[7] if extrapolated to the temperature of the arc, predict a current density nearly a million times greater. These early experiments of Richardson

[1] Electric Arcs.
[2] Roy. Soc. Proc., A, 47, p. 123, 1890.
[3] Roy. Soc. Proc., A, 92, p. 122, 1915.
[4] Conduction of Electricity through Gases, 2d ed., p. 604.
[5] Roy. Soc. Proc., A, 97, p. 326, 1920.
[6] Electric Arcs, p. 164.
[7] Phil. Trans., 201 A, p. 497, 1903.

were, however, made under quite unsatisfactory conditions, so that he has revised his values for the constants in the thermionic equation. The best present evidence on thermionic emission from carbon, as will be discussed later in the paper, indicates that thermionic currents of the order of the observed arc currents are to be expected at the temperature of the arc, so that this objection to Thomson's theory seems unfounded.

A second objection is suggested in the fact that, in the mercury arc, the cathode would vaporize at a temperature far below that required to give appreciable thermionic emission. It has been pointed out by Stark,[1] however, that there is an incandescent spot on the surface of the mercury cathode, indicating that local high temperature can be reached before the atoms have time to evaporate from the liquid surface. Thus this argument is inconclusive.

Pring[2] performed experiments which appeared to indicate that the electronic emission from incandescent carbon is dependent on the presence of gases capable of chemical action on the hot carbon and vanishes to the extent to which such gases are removed. Richardson,[3] however, showed that the nature of Pring's results was entirely accounted for by the effect of the magnetic field of the current used in heating his carbon cathode, together with the effect of gases on the mean free paths of the ions. Thus Pring's experiments do not really bear on the vital problem of the arc.

Ionization of the cathode as a direct result of impacts of positive ions which have fallen through the cathode drop of potential is a suggested source of electronic emission from the cathode.[4] It is argued that, although bombardment of cold cathodes produces no detectable electronic emission at voltages similar to those in the arc, yet such emission may occur if the cathode is at a high temperature. However, the fact that the work done during the escape of an electron from the surface of a conductor is found to be practically independent of the temperature[5] would seem to make this view untenable.

The theory discussed in the preceding paragraph has recently been upheld by Bräuer,[6] who describes experiments and calculations which lead him to conclude (1) that thermionic emission accounts for only a few per cent of the total arc current, and the ionization produced by thermoelectrons constitutes a negligible fraction of the current and (2)

[1] Phys. Zeit., 5, p. 750, 1904.
[2] Roy. Soc. Proc., 89 A, p. 344, 1913.
[3] Roy. Soc. Proc., 90 A, p. 174, 1914.
[4] Child, Electric Arcs, p. 165.
[5] Richardson, Emission of Electricity from Hot Bodies, pp. 164–178; Koppius, PHYS. REV., 18, p. 443, 1921.
[6] Ann. d. Physik, 60, p. 95, 1919.

that the electronic emission is due principally to the impact of positive ions against the cathode, the high temperature of the cathode so reducing the work necessary to extract an electron that each impinging positive ion is able to eject a large number of electrons.

I think Bräuer's interpretation of his results can be shown to be impossible, and that they can readily be explained in a manner quite compatible with Thomson's theory of the thermionic origin of the primary current of the arc.

In the remainder of this paper I shall discuss (1) the adequacy of thermionic emission as the source of the electron current in an arc, (3) the interpretation of Bräuer's experiments, (4) the theory of the arc. In connection with Bräuer's experiments it will be necessary to discuss (2) the limitation of thermionic emission by space charge.

## I. The Adequacy of Thermionic Emission as the Source of the Electron Current in an Arc.

### (*a*) *Carbon Arcs.*

The thermionic emission from the cathode of an arc may come from its entire surface, but by far the greater part of it must proceed from the cathode "spot," whose temperature is higher than that of the rest of the cathode. Its temperature is 3,140° K according to Reich,[1] and its diameter is such as to lead to estimates of the total current density at this point of the arc varying from 180 to 318 amperes per sq. cm.[2] Child's estimate of thermionic current density at this temperature, giving a value of $2(10)^8$ amps. per sq. cm, was based on constants of thermionic emission which are now known to be much in error.[3] Bräuer, on the other hand, calculates the thermionic emission using data published in a preliminary note by Langmuir and finds the expected emission to amount to only 1.2 amps. per sq. cm at 3,500° K. Unfortunately, however, these data are also incorrect, owing, presumably, to a printer's error, since they were added in a note with the proof.

Langmuir's values for the constants $A$ and $b$ of Richardson's equation for the thermionic current

$$N = A\sqrt{T}\,\epsilon^{-b/T} \qquad (1)$$

were determined under conditions of the best vacua attainable in a "baked out" tube immersed in liquid air and with a vaporized metallic deposit on the glass bulb.[4] They are by far the most reliable data

[1] Phys. Zeit., 7, p. 73, 1906.

[2] Granqvist, Phys. Zeit., 4, p. 537, 1903; Reich, Phys. Zeit., 7, p. 73, 1906.

[3] Richardson, Emission of Electricity from Hot Bodies, p. 75.

[4] Am. Electrochem. Soc. Trans., 29, p. 125, 1916; Richardson, Emission of Electricity form Hot Bodies, p. 69.

available. From them are calculated the thermionic current densities for pure carbon in Table I.

TABLE I.

| Carbon. $A = 1.49(10)^{25}$. $b = 48{,}700$. | | Lime-Impregnated Cathode. $A = 3.3(10)^{26}$. $b = 42{,}000$. | |
|---|---|---|---|
| $T°$ K. | Amps./cm². | $T°$ K. | Amps./cm². |
| 2,700 | 1.9 | 2,700 | 500 |
| 3,000 | 13.2 | 3,000 | 2,390 |
| *3,140 | 26.7 | 3,140 | 4,400 |
| 3,300 | 54.7 | | |
| 3,500 | 127 | | |
| 4,000 | 775 | | |

Two points must be borne in mind. In the first place the temperature of the cathode bright spot is not known very accurately. Bräuer makes his comparison on a basis of 3,500° K. It is known in a qualitative way only that the temperature is higher when pure carbon electrodes are used than when the carbon contains impurities of an electropositive nature. In the second place, arc carbons are inevitably contaminated by materials of a more electropositive nature, such as calcium and sodium, which are known greatly to increase the thermionic emission even when present in minute quantity. In a carbon arc, the volatilization of the cathode continually presents new surface, so that the electrode never can be completely freed from these impurities by continued heating, as could be done with the filaments used in Langmuir's experiments. Table I. also shows calculated current densities from cathodes coated with CaO, the constants of the Richardson formula being averages of the closely agreeing values given by Deininger, Wehnelt and Jentzsch.[1]

In view of these considerations it seems safe to estimate the thermionic emission from the cathode of a carbon arc as lying between the values given in Table I. at the appropriate temperature. It is evident that the thermionic current is at least an important part of the total current, and there is no reason for believing that it is not practically the total current.

### (*b*) *Arcs between Tungsten Electrodes.*

Bräuer again belittles the rôle played by thermionic emission by calculations based on experiments of Mackay and Ferguson[2] on arcs between tungsten electrodes in hydrogen at pressures of about 400 mm. They state that the arc was about 0.5 mm in diameter when the current

[1] Richardson, Emission of Electricity from Hot Bodies, p. 81.

[2] Frank. Inst. Jour., 191, p. 209, 1916.

was 25 amps. Thence Bräuer calculates a current density of 3,200 amps./cm², which much exceeds the possible thermionic current density.

Mr. Mackay has kindly informed me, however, that the dimension of 0.5 mm referred to the luminous line of the discharge between the electrodes and not to the size of the hot tungsten cathode, which was a tungsten button whose surface area was approximately 0.5 cm² and whose temperature at the hottest part was not less than 3,300° K. Although the most intense thermionic emission must have come from this hottest spot, the remaining larger area of the hot cathode must have contributed considerably to the total current. If the current had come equally from the entire area, the current density would have been 50 amps./cm² instead of 3,200. By determining pyrometrically the actual distribution of temperature over the surface of the cathode, the investigators concluded that the expected thermionic currents equalled the arc currents except in the case of the peculiar intense line discharge obtained at high gas pressures, in which case the arc current was larger than the expected thermionic current, but of the same order of magnitude.

Table II. gives actual thermionic currents from tungsten, using Langmuir's data.[1] More recent data for pure tungsten give currents a little lower, but those given in the table are probably applicable to comparison with the arc currents between the tungsten buttons used.

TABLE II.

Tungsten: $A = 1.55(10)^{26}$.
$b = 52{,}500$.

| $T°$K. | Amps./cm². |
|---|---|
| 2,400 | 0.365 |
| 2,800 | 8.98 |
| 3,200 | 96.9 |
| 3,540 M.P. | 509 |

### (*c*) *Low Voltage Arcs.*

In this laboratory recent experiments on low voltage arcs in helium, hydrogen, mercury vapor, nitrogen and iodine, stimulated by thermionic bombardment from an independently heated tungsten cathode, have led us to the conclusion that the current in this type of arc is the thermionic current, limited to a greater or less extent by the space charge. The ionization in the arc functions principally in providing positive ions, each of which permits the liberation of many additional electrons because it moves relatively slowly through the region of the space charge. On this view, the maximum current through a low voltage arc (one in which

[1] Mackay and Ferguson, loc. cit.

the voltage is insufficient to permit an electron to ionize more than once on its path between the electrodes) should never exceed twice the saturation value of the thermionic emission, and should ordinarily be less than this.

The following experimental results may be cited as examples. In mercury vapor at 3 mm pressure an arc current of 15 amps. was observed at 8 volts difference of potential between the electrodes. The cathode was a coil consisting of three close turns of 20-mil tungsten wire, wound around a 20-mil iron wire which was then dissolved away. Beyond the coil, on each side, was a 3-mm length of the tungsten which was welded to stout molybdenum leads which carried in the heating current of about 24 amperes. Because of its shape, the coil of three turns was heated to a higher temperature than the straight connecting wires, so that we may assume, to a first approximation, that the total thermionic emission comes from this coil. The effective emission area may be calculated approximately by considering it to be a drum of 60 mils length and 60 mils external diameter, giving a surface area of 0.106 $cm^2$. The temperature of the coil was not measured, owing to the difficulty of using any method of measuring such high temperature while the arc current was flowing. The middle one of the three turns must have been near the melting point of tungsten, however, since the wire became thinner and soon burned out at this point. (It is not likely that this burning out was due to chemical action on the filament, since, at a slightly lower temperature, the resistance of the wire remained constant for hours.) In view of some experience in measuring temperatures of similar coils by their resistances in the absence of ionization, I feel safe in estimating the mean temperature of the coil as between 3,200° K and 3,400° K. The current density was about 142 amps./$cm^2$, which falls within the range to be expected from thermionic emission from tungsten at the estimated temperatures.

Similar experiments were made in helium at pressures up to 10 mm. In this case the maximum current densities obtained were about 60 amps./$cm^2$. Here the temperature was not quite as high as in the case of mercury, because it was desired to conserve the filament for a series of spectroscopic observations.

Current densities of about the same magnitude, though slightly smaller, were observed in hydrogen, nitrogen and iodine arcs. In the case of nitrogen, the currents became abnormally large when the "flare," due to dissociation of nitrogen, set in.[1] This was probably due to the decreased proportion of the applied voltage which occurred outside the region of the cathode drop, owing to the increased conductivity of the gas, or to

[1] Duffendack, PHYS. REV., 20,665, 1922.

the chemical action of atomic nitrogen on the filament. Even in this case, however, the current densities did not exceed the possible thermionic currents given in Table II.

It may be noted, in passing, that the considerations advanced above are not vitiated by the effect of gases on the constants of thermionic emission from tungsten, for Langmuir [1] has shown that these effects, which are large at lower temperatures, become of less importance at higher temperatures and are probably negligible at the highest temperatures reached by the tungsten.

In view of these facts it is difficult to escape the conviction that thermionic emission from the cathode is adequate to account for the primary current of the arc. At any rate the "burden of proof" to the contrary must rest upon those who advocate a different source of current. Bräuer interpreted his experiments as constituting such a proof. Before discussing his experiments it is necessary to examine conditions which limit the current from an electrode at a high temperature in a gas.

## II. The Limitation of Current by Space Charge.

In his book "Conduction of Electricity through Gases," Sir J. J. Thomson called attention to the effect of the space charge, due to ions, on the distribution of potential between electrodes. Langmuir [2] applied this principle to the emission of electrons from a hot cathode, and showed that the current density $i_v$ between plane parallel electrodes in *vacuo* is limited to the value

$$\begin{aligned} i_v &= \frac{\sqrt{2}}{9\pi}\sqrt{\frac{e}{m}}\frac{V^{3/2}}{d^2} \\ &= 2.33(10)^{-6}\frac{V^{3/2}}{d^2}\ \text{amps./cm}^2. \end{aligned} \tag{2}$$

Richardson and Bazzoni [3] showed that the current density $i_e$ in a gas in which the electrons make elastic impacts with the molecules is similarly limited to

$$\begin{aligned} i_e &= \frac{\sqrt{2}}{4\pi}\sqrt{\frac{e}{m}}\frac{\lambda}{d}\frac{V^{3/2}}{d^2} \\ &= 5.24(10)^{-6}\frac{\lambda}{d}\frac{V^{3/2}}{d^2}\ \text{amps./cm}^2. \end{aligned} \tag{3}$$

In these equations $V$ is the difference of potential between parallel plates distant $d$ apart, $\lambda$ is the mean free path of an electron through the gas and $e/m$ is the ratio of the charge to the mass of an electron.

[1] Phys. Rev., 2, p. 457, 1913.
[2] Phys. Rev., 2, p. 457, 1913.
[3] Phil. Mag., 32, p. 426, 1916.

In a gas in which electrons make inelastic impacts with molecules the limiting current density $i_i$ may be calculated as follows:

$$\frac{d^2V}{dx^2} = 4\pi\rho,$$

where $x$ is measured outward from the surface of the cathode. The density of space charge $\rho$ at any point is $\rho = i/v$, and the average velocity of the electrons $v$ is easily shown to be

$$v = \sqrt{\frac{\pi e\lambda}{2m}\frac{dV}{dx}}.$$

With these substitutions,

$$\sqrt{\frac{dV}{dx}\frac{d^2V}{dx^2}} = 4\pi i\sqrt{\frac{2m}{\pi e\lambda}}.$$

This is integrated twice and the integration constants determined by the fact that the current is limited to such a value as makes $dV/dx = 0$ when $x = 0$ and by the relations $V_{x=0} = 0$, $V_{x=d} = V$. In this way, and putting $i = i_i$, we obtain

$$\begin{aligned} i_i &= \frac{1}{4\sqrt{2\pi}}\left(\frac{10}{9}\right)^{3/2}\sqrt{\frac{e}{m}}\sqrt{\frac{\lambda}{d}}\frac{V^{3/2}}{d^2} \\ &= 5.45(10)^{-6}\sqrt{\frac{\lambda}{d}}\frac{V^{3/2}}{d^2}\ \text{amps./cm}^2. \end{aligned} \qquad (4)$$

## III. Interpretation of Bräuer's Experiments.

Bräuer suddenly short-circuited an arc through a resistance of such size as to reduce the difference of potential between the electrodes to a value, such as 10 volts, too small to maintain ionization of the gas between the electrodes. An oscillograph in the arc circuit measured the current before and after thus suddenly reducing the voltage. It was found that the current between the electrodes dropped, practically instantaneously, to a small percentage of its value before the short-circuiting switch was thrown. This percentage was 1 to 3.5 with pure carbon electrodes, 4 to 5 with cored carbons containing some salts and oxides, 8 to 12 with carbons impregnated with $CaF_2$ and 1.5 to 1.8 in the case of a mercury arc.

Bräuer believes that the small current which persists after short-circuiting the arc is the true thermionic current, which he therefore takes to be but a small fraction of the total arc current. He points out that the electrodes are still at practically the normal arc temperature, and argues that these small currents are true saturation thermionic currents.

The conclusion that they are saturation currents is based on the experimental fact that they are practically independent of changes in the arc length which would vary the electric intensity by a factor of two or three.

That this interpretation of the results is impossible, I believe is shown by Table III., which shows the maximum possible current densities permitted by the space charge under the conditions appropriate to equations (2), (3) and (4). The mean free path $\lambda$ of an electron is known to be given with considerable accuracy by the relation $\lambda = 4\sqrt{2}\,L$, where $L$ is the mean free path of a gas molecule. Taking $L$ as $9.6(10)^{-6}$ cm for air under standard conditions, and reducing to a temperature of 2,730° K, as a rough estimate of the temperature of the gas near the cathode after the arc has been shut off, we find $\lambda = 0.54(10)^{-3}$ cm.

TABLE III.

Limiting Current Densities: $i_v$ in a vacuum,
$i_e$ in an elastic gas,
Taking $V = 10$ volts. $i_i$ in an inelastic gas.

| $d$ (cm). | $i_v$ (amps./cm²). | $i_i$ (amps./cm²). | $i_e$ (amps./cm²). |
|---|---|---|---|
| 0.2 | $1.87(10)^{-3}$ | $0.223(10)^{-3}$ | $0.0112(10)^{-3}$ |
| 0.4 | 0.47 | 0.039 | 0.0014 |
| 0.6 | 0.21 | 0.014 | 0.00041 |
| 0.8 | 0.12 | 0.007 | 0.00018 |
| 1.0 | 0.075 | 0.004 | 0.00009 |

Even in a perfect vacuum the maximum possible thermionic currents would have been at least a thousand times less than those which Bräuer observed, because of the limitation by space charge. Under his actual conditions, in air, the currents would have been much less still, ranging between the values of $i_i$ or $i_e$ according to the degree of elasticity of impact of electrons with air molecules at high temperatures. As far as our evidence goes, the values of $i_i$ are probably the more nearly appropriate. It is evident, therefore, that *Bräuer did not measure the thermionic current of an arc, and hence that his experiments cannot be taken as evidence against the theory that the principal part of an arc current is of thermionic origin.*

A reasonable explanation of Bräuer's results can be suggested along the following lines, which are quite in conformity with the idea of the thermionic origin of the primary arc current. The electrodes are at a sufficiently high temperature to give a large thermionic current, but this is limited by space charge. The only way to obtain currents larger than those given in Table III. is by supplying positive ions, each of which permits the escape of many additional electrons, as the following calculation shows.

Ions, whose mean free path $l$ is considerably less than the distance between the electrodes, are drawn through a gas by an electric intensity $E$ with an average velocity of drift [1]

$$v \propto l\Omega eE,$$

where $\Omega$ is the average translational velocity of the ion. At any point in the field the product $eE$ is identical (except in sign) for electrons and positive ions, since it is safe to assume the ions to be singly charged under the conditions of the experiments. $\Omega$ for an electron is $\sqrt{1,836M}$ times $\Omega$ for an ion, $M$ being the molecular weight of the ion. $l$ for an electron is $4\sqrt{2}$ times $l$ for an ion, the factor 4 arising from the negligible size of the electron and the factor $\sqrt{2}$ from the fact of its much greater speed. Thus the electrons drift through the gas $4\sqrt{3,672M}$ times faster than do the positive ions. Since the contribution of an ion to the space charge varies inversely as its velocity of drift, it is seen that each positive ion neutralizes the space charge of $242\sqrt{M}$ electrons and thus permits the escape of that additional number, provided the cathode is hot enough to supply them.

In Bräuer's experiments with the carbon arc the voltage was insufficient to produce positive ions in the gas. The hot anode, however, was certainly a source of a plentiful supply, since the greatest care and long heat treatment are required to eliminate positive emission even from thin strips of carefully purified metals. In his experiments with impregnated carbons, the positive emission must have been particularly large.

It is impossible accurately to calculate the positive emission under the conditions of Bräuer's experiments, but a rough estimate of its probable order of magnitude may be made. For platinum in air approximate values are given in Table IV. For heated salts the currents are

TABLE IV.

Platinum in Air.[2] $A = 7(10)^{18}$. $b = 24{,}600$.

| $T°$ K. | $i_+$ amps./cm$^2$. |
|---|---|
| 2,000 | 0.00022 |
| 2,500 | 0.0029 |
| 3,000 | 0.017 |
| 3,500 | 0.058 |

usually larger, especially at the lower temperatures. The data for carbon are unknown, but the currents would probably be somewhat less than

[1] See equation (12) of this paper.

[2] Richardson, Emission of Electricity from Hot Bodies, p. 218.

these if the carbon could be purified, but would be of this order of magnitude if the carbon contained impurities.

Now the area of the anode crater is of the order of 1 $cm^2$, but only those positive ions which happened to enter the cathode in the region of the "bright spot" would be effective in neutralizing space charge. Probably the effective positive currents would be of the order of 1/10 of the values given in Table IV. The average atomic weight of the positive ions would certainly be close to 40, as shown by Richardson's experiments. Thus the positive emission from the anode would give rise to an electronic current from the cathode about 1,500 times as large as itself and quite adequate to account for Bräuer's experiments.

It is evident, therefore, that an experimental arrangement such as Bräuer employed would measure not the thermionic emission from the cathode but the positive emission from the anode, magnified about 1,500 times by the resultant liberation of electrons.[1] His observation that the currents were approximately independent of arc length is to be expected in view of the fact that the space charge remained negative, so that the positive emission would reach approximately its saturation value for all arc lengths.

## IV. Theory of the Arc.

It is difficult to formulate a theory of the arc because the complexity of the phenomena makes it difficult to distinguish its essential features from those of secondary or accidental significance. A study of the simplest arcs, low voltage arcs between independently heated non-vaporizing electrodes in gases at reduced pressures,[2] has made it fairly certain that the essential feature of an arc is an emission of electrons from the cathode which produce sufficient ionization of the surrounding gas to give a positive space charge just outside the cathode, thus permitting approximately saturation electron emission at relatively low voltage. All other characteristics of arcs appear to be either consequences of this emission and ionization or prerequisites to it under the particular physical conditions in which the arc is produced. Thus it is possible to produce arcs in which the anode drop in potential is practically eliminated, in which the potential gradient in the gas between the electrodes is nearly zero, in which there is no chemical action or consumption of the electrodes or the gas, or in which the gas and anode temperatures are low. The cathode drop and its emission of electrons are, however, indispensable.

[1] Recent experiments by Professor A. Trowbridge and the writer have proved the correctness of this explanation of Bräuer's results.

[2] Mackay and Ferguson, loc. cit.; Compton, Olmstead and Lilly, Phys. Rev., 16, p. 282, 1920; Duffendack, Phys. Rev., loc. cit.

(*a*) *Conditions at the Cathode.*

If $i$ is the current density of the negative emission from the cathode, there must be a current density $j$ of positive ions sufficient to neutralize the space charge of the electrons. As we have seen,

$$i = 242\sqrt{M}\, j, \tag{5}$$

where $M$ is the molecular weight of the positive ions. Besides these, there must be an additional positive current density $J$ to give the excess positive space charge, to which the cathode drop is due. Let $\rho$ be the density of the space charge.

$$\frac{d^2V}{dx^2} = -4\pi\rho = -4\pi\frac{J}{v}.$$

$v$ is the average velocity of drift of the positive ions and is given by

$$v = \sqrt{\frac{\pi e}{2m} l \frac{dV}{dx}},$$

where $e/m$ is the ratio of charge to mass and $l$ is the mean free path of the positive ions. This expression is based on the assumption that the ion loses its forward velocity at each collision which must, on the average, be approximately true since ions and molecules have approximately equal masses. Thus, putting

$$B = \frac{4\pi}{\sqrt{\frac{\pi e}{2m} l}},$$

$$\sqrt{\frac{dV}{dx}}\frac{d^2V}{dx^2} = -BJ,$$

$$\left(\frac{dV}{dx}\right)^{3/2} = -\tfrac{3}{2}BJx + C_1.$$

The integration constant $C_1$ is determined by the condition that $dV/dx = 0$ (approximately) at the boundary of the cathode drop—at a distance from the cathode which we shall call $c$. Thus

$$\frac{dV}{dx} = [\tfrac{2}{3}BJ(c - x)]^{2/3}.$$

Integrating again,

$$V = -(\tfrac{2}{3}BJ)^{2/3}\tfrac{3}{5}(c - x)^{5/3} + C_2.$$

Since, when $x = 0$, $V = 0$ and when $x = c$, $V = V_c$, where $V_c$ is the cathode drop in potential, we have

$$V_c = \tfrac{3}{5}(\tfrac{2}{3}BJ)^{2/3}c^{5/3}.$$

Substituting the value of $B$, we have

$$V_c = \frac{3}{5} \frac{\left(\frac{8\pi}{3}\right)^{2/3} J^{2/3} c^{5/3}}{\left(\frac{\pi}{2} \frac{e}{m} l\right)^{1/3}} \tag{6}$$

as the value of the cathode drop of potential.

It has been well established that the minimum value of $V_c$ is the minimum voltage through which an electron must fall in order to ionize the surrounding gas. This is not always the "minimum ionizing potential," which refers to the voltage necessary to ionize at a single impact, since ionization may be a cumulative effect of two or more impacts. If the gas molecules are multi-atomic, this minimum voltage is probably identical with the "minimum ionizing potential." [1] If they are monatomic, it may be the "minimum radiating potential" [2] or the difference between the minimum ionizing and minimum radiating potentials.[3] In any case, the minimum values of $V_c$ are pretty well established in several cases (5.5 volts in the mercury arc, 8.6 volts in the carbon arc, 16.2 volts in a tungsten arc in hydrogen, etc.). These minimum values of $V_c$ are found when the arc operates under conditions favorable to ease of operation and passage of good sized currents. Under these favorable conditions, therefore, we may consider $V_c$ as a known quantity.

As far as the writer is aware, no accurate measurements of the thickness of the region of cathode drop $c$ in arcs have been made. Theoretical considerations, however, indicate that it should be about equal to the mean free path of the electrons from the cathode, since these have their best chance of ionizing at their first impact, owing to the fact that the electric intensity diminishes with distance from the cathode. This is almost certainly true in gases in which electrons lose their energy at each impact, such as multi atomic gases or monatomic gases whose molecules are partially ionized by previous impacts or absorption of radiation. This conclusion is strengthened by measurements of the thickness of the cathode drop in Geissler tube discharges, in which the width is found to be equal to the electronic free path with probably as much accuracy as the free paths are known at the large velocities involved. We shall, therefore, assume that $c$ equals the electronic mean free path $\lambda$, *i.e.*, that $c = 4\sqrt{2}\, l = \lambda$.

This leaves $J$ as the only unknown quantity, and its value may there-

[1] Duffendack, loc. cit.

[2] Compton, Olmstead and Lilly, loc. cit.

[3] Yao, PHYS. REV., 21, 1, 1923.

fore be determined. We find

$$J = \frac{3}{16\pi}(\tfrac{5}{8}V_c)^{3/2}\left(\frac{\pi}{2\sqrt{2}}\frac{e}{m}\right)^{1/2}\frac{1}{\lambda^2} = 1.47(10)^{-7}\frac{V_c^{3/2}}{M^{1/2}\lambda^2}\text{ amps./cm}^2, \quad (7)$$

where $V_c$ is expressed in volts, $M$ is the molecular weight of the positive ion, and $\lambda$ is the electronic mean free path.

An application of this expression to various cases leads to reasonable values for $J$. It must be remembered that some of the data are not known with certainty, so that proper orders of magnitudes only can be expected.

1. *Carbon Arc.*—At atmospheric pressure and 3,300° K, which is close to the temperature at the cathode, we find $\lambda = 0.66(10)^{-3}$ cm. We have $V_c = 8.6$ volts and we may take $M = 16$ to at least the right order of magnitude. We then find, by equation (7), that $J = 2.5$ amps./cm². Since 250 amps./cm² is an average value for the current density of the arc current at the cathode, we have about 0.01 of the total current due to the *excess* positive current, which is in addition to the fraction $1/242\sqrt{M}$, or about 0.001, which just neutralizes the electronic space charge. Thus about 0.011 of the total current is carried by positive ions.

2. *Hydrogen Arc.*—(*a*) Taking data from the work of Mackay and Ferguson, we have pressure = 400 mm., $T = 3{,}300°$ K, whence $\lambda = 2.4(10)^{-3}$ cm according to kinetic theory. In hydrogen, however, we know from the work of Loeb [1] that the actual free path of an electron is only 0.53 of its theoretical value, so that our best value for $\lambda$ is $1.27(10)^{-3}$ cm. $V_c = 16$ volts and $M = 2$. Thus $J = 4.1$ amps./cm². The observed current density was about 75 amps./cm², so that about 0.055 of the total current was due to *excess* positive ions and $1/242\sqrt{2}$ to *neutralizing* ions. Thus about 0.058 of the total current was carried by positive ions.

(*b*) From data taken in this laboratory with an arc in which the cathode was independently heated, we had, at 5 mm. pressure of hydrogen, an estimated temperature of 3,000° K and a current density of about 20 amps./cm², giving $J = 8(10)^{-4}$ amps./cm²; whence $0.00004 + 0.003 = 0.003$, approximately, is the fraction of the total current which was carried by positive ions.

3. *Mercury Arc.*—The temperature of the vapor near the cathode of an arc is unknown. If the arc is maintained by an independently heated tungsten cathode, or by a self-heated tungsten cathode as in one type of

[1] PHYS. REV., 20, p. 106, 1922.

Cooper-Hewett quartz-mercury arc, the temperature is probably at least 2,800° K. In an ordinary arc with a mercury cathode, the temperature of the "bright spot" is unknown. It is probably at least 2,000° K. An assumed temperature of 1,000° K cannot be wrong by a factor more than three. $V_c = 5.5$ volts and $M = 200$.

If $p = 1$ mm, $\lambda = 0.049$ cm, and $J = 0.056(10)^{-3}$ amps./cm$^2$. The area of cross section of the cathode bright spot is unknown, but, in a well-known type of arc such as the Hereaus, cannot exceed 0.05 cm$^2$. If the total current is 3 amperes, the current density is at least 60 amps./cm$^2$, so that the *excess* positive current would be $9(10)^{-7}$ of the whole. The *neutralizing* current is $1/242\sqrt{200} = 0.29(10)^{-3}$ of the total. Thus about 0.0003 of the total current is carried by positive ions.

If $p = 100$ mm, $\lambda = 0.00049$ cm and $J = 0.56$ amps./cm$^2$. In this case 0.0093 of the total current is carried by positive ions.

If $p = 760$ mm, $\lambda = 0.000065$ cm and $J = 32.5$ amps./cm$^2$. Here a little more than half the assumed current would be carried by positive ions. This is physically impossible, which probably means than an arc would not maintain itself at 3 amperes under 760 mm. pressure—a lower pressure or higher current being required.

From the above examples it is seen that the least fraction of the current carried by positive ions is $1/242\sqrt{M}$, and that this occurs only at very low gas pressures. At the highest pressures, on the other hand, the large value of $J$ sets a lower limit to the possible arc current, since the total arc current must exceed $2J$.

### *Energy Considerations at Cathode.*

In addition to satisfying the space charge relations, the conditions at the cathode must satisfy the principle of conservation of energy. This was long ago pointed out by J. J. Thomson,[1] but has not always been taken into account. In the light of our present knowledge the energy relations at the cathode may be formulated as follows:

Let $n_1$ and $n_2$ be the numbers, respectively, of electrons leaving the cathode and of positive ions reaching it per second. If $e\phi$ is the heat of evaporation of an electron from the cathode,[2] the cathode loses heat at the rate of $n_1 e\phi$ as a result of thermionic emission. It likewise gains heat at the rate of $n_2 e V_c$ from the energy gained by the positive ions in falling through the cathode drop of potential $V_c$.

$(n_1 - n_2)$ electrons fall through the cathode drop without ionizing. Their energy is, of necessity, dissipated ultimately in the form of heat.

[1] Conduction of Electricity through Gases, 2d ed., p. 614.

[2] Richardson, Emission of Electricity from Hot Bodies, p. 164.

Since this occurs close to its surface, the cathode gains half of this energy, or $\frac{1}{2}(n_1 - n_2)eV_c$, provided the mean free path is small in comparison with the linear dimensions of the emitting surface of the cathode. In general we have $f(n_1 - n_2)eV_c$, where $f$ is the fraction of the total solid angle, about a point distant $\lambda$ from the cathode, which is subtended by the cathode.

When positive ions are absorbed into the cathode, some energy is liberated in addition to the kinetic energy with which they strike. This includes (1) heat of condensation of positive electricity, (2) heat of condensation of the uncharged material of the ion, (3) possible chemical action. Its amount may be taken account of by imagining the absorption of the positive ions to proceed in the following way. An electron escapes from the cathode, absorbing heat $e\phi$, and combines with the positive ion outside the surface, liberating heat $eV_i$ where $V_i$ is the ionizing potential of the gas. The neutral system is then absorbed by the cathode, liberating heat $L$, where $L$ is the latent heat of condensation per molecule, or the heat of chemical combination per molecule. Thus $n_2[e(V_i - \phi) + L]$ is the rate at which heat is liberated by absorption of positive ions.

Finally, there are other heat losses which may be grouped as $(C + C' + R - H)$, where $C$ is loss by conduction through the cathode, $C'$ is loss through the gas, $R$ is net loss by radiation and $H$ is heat supplied by independent heating of the cathode, if it be electrically or otherwise heated. In a self-maintained arc $(C + C' + R)$ represents a positive heat loss. If the cathode is independently heated, $(C + C' + R - H)$ may be positive or negative, depending on conditions.

Grouping all these items, we find the equilibrium condition to be given by

$$n_2eV_c - n_1e\phi + f(n_1 - n_2)eV_c + n_2e(V_i - \phi) + n_2L - C - C' - R + H = 0,$$

or

$$\frac{n_2}{n_1} = \frac{\phi - fV_c + \dfrac{C + C' + R - H}{en_1}}{V_i + fV_c - \phi + \dfrac{L}{e}}. \tag{8}$$

In some cases the quantities in this expression are known or may be calculated with sufficient accuracy to permit an estimate of the ratio $n_2/n_1$. It is of interest to compare these estimates with those previously made from space charge considerations.

1. *The Carbon Arc.*—In this case $H = 0$. It is found that chemical action, as with introduction of oxygen, has an effect on the arc but is

not essential to its maintenance, and probably does not ordinarily play an important rôle. In such cases $L/e$ has to do with heat of condensation. In all cases where the value of $L/e$ is known it is much smaller than the other terms in equation (8), so that we shall neglect it. $V_c = 8.6$ volts and $\phi = 3.92$ volts for carbon. $V_i$ is uncertain, because the kind of atom which is principally ionized in the ordinary arc in air is unknown. For most substances, including oxygen and nitrogen, $V_i$ is about 16 volts. We will therefore put $V_i = 16$ volts provisionally. $f = 1/2$.

If we neglect the losses $(C + C' + R)$ we obtain a minimum value for $n_2/n_1$ of $n_2/n_1 > -0.0244$, which means, of course, that $n_2/n_1 > 0$.

A probable maximum limit to $n_2/n_1$ can be found by using Richardson's conclusion that, at temperatures above 3,000° K the cooling effect due to evaporation of a saturation current of electrons exceeds that due to radiation, which is easily shown to be the major term in $(C + C' + R)$. Thus

$$\frac{C + C' + R}{en_1} < \phi,$$

and an upper limit to $n_2/n_1$ is given by

$$\frac{n_2}{n_1} < \frac{2\phi - \frac{1}{2}V_c}{V_i + \frac{1}{2}V_c - \phi} = 0.215.$$

Thus

$$0 < \frac{n_2}{n_1} < 0.215.$$

A closer estimate may be made by attempting to evaluate $(C+C'+R)$. Taking a current of 10 amps., the area of the bright spot is about 0.04 cm², the temperature gradient is of the order of 2,500 deg./cm and the conductivity is about 0.01. Reducing to appropriate units we find $C/n_1e = 0.04$ volt, approximately.

Since the temperature of the surrounding gases exceeds that of the cathode, $C'$ is negative, but rough calculations show it to be negligible compared with $C$ and $R$. If the cathode is cooled by convection, as by blowing it, $C'$ may become positive and large. It seems safe, however, to neglect $C'$ under ordinary conditions.

The loss by radiation is calculated by assuming both anode and cathode to radiate as black bodies at the rate of $5.5(10)^{-5}T^4$ ergs/cm² sec. Taking the cathode to be at 3,140° K we find its loss to be at the rate of 21.3 watts, approximately. This loss is reduced, however, by a gain of heat from the anode, whose crater usually subtends about one third of the hemi-solid angle about the cathode spot, and whose temperature is about 3,700° K. Thus, in exchange for the 7.1 watts radiated to the

anode crater, $7.1\left(\frac{3,700}{3,140}\right)^4 = 13.8$ watts are returned. The net loss from the cathode is thus $21.3 - 13.8 = 7.5$ watts, whence $R/n_1e = 0.75$ volt, approximately.

Combining these terms $(C + C' + R - H)/n_1e = 0.79$ volt. Substituting this value in equation (8) gives

$$\frac{n_2}{n_1} = 0.025, \qquad \text{whence} \qquad \frac{n_2}{n_1 + n_2} = 0.0245,$$

as the best estimate which we can make. The previous method gave a value 0.011. The difference is well within the limits to be expected in view of the uncertain data upon which the calculations are based.

2. *Hydrogen Arc between Tungsten Electrodes.*—(*a*) Here the data are more accurately known. $V_i = 16$ volts, $\phi = 4.4$ volts, $V_e = 16$ volts. In the work of Mackay and Ferguson, $T = 3,300°$ K, current = 25 amps. and effective area = 0.375 cm², approximately. Thus $R = 141$ watts and $R/n_1e = 5.6$ volts, approximately. Owing to the construction of the apparatus $C$ may be neglected, $C'$ is small compared with $R$ and $H$ is zero. Thus we have

$$\frac{n_2}{n_1} = 0.102, \qquad \text{whence} \qquad \frac{n_2}{n_1 + n_2} = 0.091$$

as compared with 0.058 calculated for the same case by the previous method.

(*b*) In dealing with the second example of hydrogen, we must take $f = 1/6\pi$, approximately, since the mean free path at $T = 3,000°$ K and 5 mm pressure, which is 0.09 cm, caused the energy of the electrons to be liberated at a distance at which the wire (15 mil) subtended about $1/6\pi$ of the total solid angle. The emitting area of the cathode was, in this case, estimated as 0.3 cm². We thus calculate $R/n_1e$ to be approximately 2.23 volts.

If we neglect the independent heating $H$ we find

$$\frac{n_2}{n_1} = 0.52, \qquad \text{or} \qquad \frac{n_2}{n_1 + n_2} = 0.34.$$

This value is nearly a hundred times greater than that calculated by the previous method, *viz.*, 0.003, which means that the arc could not be maintained under these conditions of current and pressure without independent heating of the cathode,—as was the case. If we assume that the two methods, including the value of $H$, should yield identical

results, we find that

$$\frac{n_2}{n_1} = 0.003 = \frac{4.4 - \frac{16}{6\pi} + 2.6 - \frac{H}{n_1 e}}{16 + \frac{16}{6\pi} - 4.4},$$

whence $H = 36.66$ watts. Actually, the cathode filament was heated by a current of 18 amperes with a potential drop of 3.1 volts, or 56 watts, not all of which was dissipated across the emitting part of the cathode surface. Again the two equations give consistent results.

3. *Mercury Arc.*—In this case $V_i = 10.4$ volts and $V_e = 5.5$ volts are accurately known. Probably $\phi$ is in the neighborhood of 4 volts. We cannot calculate $(C + C' + R)$ owing to ignorance of the real conditions at the surface of the cathode. If we neglect these terms, we get the lower limit for $n_2/n_1$ as

$$\frac{n_2}{n_1} > 0.123, \qquad \text{whence} \qquad \frac{n_2}{n_1 + n_2} > 0.109.$$

We previously estimated a fraction 0.0003 at 1 mm pressure, 0.0093 at 100 mm pressure and 0.54 at 760 mm pressure. The conclusion is that an arc would not maintain itself under the assumed conditions (3 amperes, cathode cross-section 0.05 cm$^2$, minimum cathode drop of 5.5 volts) unless the vapor pressure were greater than 100 mm or unless the cathode were independently heated. This agrees with experience.

From the results of these tests of the equations (7) and (8) I think there is good evidence that the essential features of the arc are those which have been incorporated in this theory of the conditions at the cathode.

### (*b*) *Conditions in the Region between the Electrodes.*

In this region the conditions may vary considerably, depending on the nature of the arc. In a low-voltage arc maintained by an independently heated cathode in a gas at a few millimeters pressure, there appears to be no ionization of gas in this region or at the anode. The region is therefore one of negative space charge, but the drop of potential across it may be very small if the anode is of large area and close. If the gas pressure is raised, the mobility of the electrons diminishes, and the space charge and potential drop increase. If the pressure is diminished considerably, there is insufficient ionization at the cathode to maintain the arc without increased voltage and, at still lower pressures, ionization by impact occurs in the region between the electrodes, and the discharge becomes one of the vacuum tube type.

*Carbon Arc.*

In the carbon arc the conditions are less simple. Experiments show that the potential gradient in this region is approximately constant, which proves that there is no space charge here. Therefore there must be sufficient ionization in this region to supply enough positive ions to neutralize the space charge of the electrons coming from the region of the cathode. We shall inquire into the origin of these positive ions by considering the various possible sources. We have seen that each positive ion neutralizes the space charge of $242\sqrt{M}$ electrons, or, roughly, 1,000 electrons. The greatest current density is near the cathode, where it amounts to about 250 amps./cm$^2$. In the middle of the arc the current density is much less, and is probably of the order of 50 amps./cm$^2$. Thus it is necessary to account for a positive current density ranging from 0.05 to 0.25 amp. per cm$^2$ in this region.

*Positive Ions from Anode.*—If these are present, they must have been produced by electron impacts on the anode and not as a result of its high temperature, since the anode may be cooled without affecting very much the conditions in the arc. But we have no independent evidence of the emission of positive ions from solids subjected to electronic bombardment at these low voltages which is at all adequate to produce the necessary positive current.

Furthermore the conditions in this region are favorable to recombination, since the potential gradient is only about 27 volts/cm and the mean free path is extremely small. The existence of recombination is proved by the luminosity of this region. Now if the positive ions originated at the anode, their number would diminish as they approach the cathode, so that the space charge could not be zero at more than one surface. Thus the anode cannot be the chief source of positive ions.

*Ionization by Collision.*—The mean free path of electrons in this region is about $0.74(10)^{-3}$ cm, assuming the temperature to be 3,700° K. With a potential drop of 27 volts/cm, an electron would fall through only 0.02 volt in an average free path. The probability of ionizing at a collision would be $\epsilon^{-V/0.02}$, where $V$ is the ionizing potential of the gas. If $V = 16$ volts, only $2.76(10)^{-347}$ of the collisions would result in ionization. Each electron makes on the order of 1,000 collisions in its path between the electrodes, so that the positive current from this cause, even neglecting all recombinations, would amount to only about $2.76(10)^{-344}$ of the electronic current.

Possibly the effective ionizing potential, by cumulative action or otherwise, is as low as 8.6 volts, as suggested by the size of the cathode drop. If we put $V = 8.6$ we find the proportion to be about $(10)^{-184}$. In either case, ionization by collision is evidently of no importance.

*Photo-electric Ionization*—This must certainly occur to some extent, since it can occur, theoretically, wherever recombination occurs. It is well known that the temperature radiation from the electrodes produces no detectable photo-electric ionization of the ordinary gases. Thus any photo-electric action, if present, must result from radiation of a very absorbable nature arising from the gas itself, and is taken account of in the following treatment.

*Thermal Ionization of Gas.*—The degree of thermal ionization may be calculated by applying Nernst's Heat Theorem after the manner of Saha.[1] We have

$$\log \frac{x^2}{1 - x^2} P = - \frac{U}{4.57T} + 2.5 \log T - 6.5, \tag{9}$$

where $x$ is the fraction of molecules ionized, $P$ is the pressure in atmospheres, $U$ is the energy required for ionization in calories per gram molecule and 6.5 is calculated from the chemical constants.

$$U = \frac{eVN}{300J} = 2.29(10)^4 V,$$

where $V$ is the effective ionizing potential in volts. $V$ is certainly not greater than 16 volts and is more likely about 8.6 volts, as evidenced by the cathode drop.

The temperature $T$ of the gases in the arc is not known at all accurately. It is agreed that it is higher than that of the electrodes.[2] Thus it may be even higher than 4,200° K.[3]

After calculating $x$ by equation (9), the number of positive ions per cm$^3$ can be calculated by multiplying $x$ by the number of molecules per cm$^3$, considering the pressure to be 1 atmosphere. Thus

$$\nu = 2.75(10)^{19} \frac{273}{T} x \tag{10}$$

is the number of positive ions per cm$^3$. It is then possible to calculate the current density $j$ of the positive ions from the relation

$$j = \nu e u E, \tag{11}$$

where $u$ is the average velocity of drift of positive ions in unit field and $E$ is the intensity of the field.

The mobility $u$ may be calculated by the principles of the Kinetic

[1] Phil. Mag., 40, p. 472, 1920.
[2] J. J. Thomson, Conduction of Electricity through Gases, 2d ed., p. 604.
[3] Lummer and Pringsheim, see Child, Electric Arcs, p. 44.

Theory. The coefficient of interdiffusion $D_{12}$ of gas 1 into gas 2 is [1]

$$D_{12} = \frac{\pi}{8N}(N_1L_1\Omega_1 + N_2L_2\Omega_2),$$

where $N_1$, $N_2$ are the numbers of molecules per unit volume; $L_1$, $L_2$ are the mean free paths; $\Omega_1$, $\Omega_2$ are the average translational velocities; $N = N_1 + N_2$. In this case the number of ions $N_1$ is so much smaller than the number of neutral molecules $N_2$ that we may neglect the first term, leaving

$$D = \frac{\pi}{8} L\Omega,$$

where $L$ and $\Omega$ refer to the molecules.

J. J. Thomson has shown [2] that the coefficient of diffusion $D$ is related to the mobility $u$ according to the equation

$$u = D\frac{Ne}{p},$$

where $p$ is the pressure of the gas.

Eliminating $D$ between these equations we have

$$u = \frac{\pi}{8}\frac{L\Omega Ne}{p}. \tag{12}$$

Substituting from (10) and (12) into (11) we find, for the positive current density,

$$j = 2.94(10)^{21}\frac{L\Omega Nxe^2E}{pT}, \tag{13}$$

or, if $j$ is in amperes and $V$ in volts,

$$j = 3.27(10)^{9}\frac{L\Omega Nxe^2E}{pT} \text{ amps./cm}^2$$

in which all the constants are accurately known and the fraction $x$ may be calculated by equation (9).

The following table shows results of calculations under several conditions, considering $L$ and $\Omega$ to be for air molecules at the temperature $T$ and atmospheric pressure. We saw that it was necessary to account

TABLE V.

| $T°$ K. | $V$ Volts. | $x$. | $\nu$. | $j$ amps./cm². |
|---|---|---|---|---|
| 3,700 ..... | 16.0 | $2.0(10)^{-10}$ | $4.0(10)^{8}$ | $5.0(10)^{-8}$ |
| 3,700 ..... | 8.6 | $2.2(10)^{-5}$ | $4.4(10)^{13}$ | $5.5(10)^{-3}$ |
| 4,200 ..... | 8.6 | $1.4(10)^{-4}$ | $2.5(10)^{14}$ | $3.5(10)^{-2}$ |
| 4,500 ..... | 16.0 | $2.5(10)^{-8}$ | $4.2(10)^{10}$ | $5.8(10)^{-6}$ |
| 4,500 ..... | 8.6 | $3.35(10)^{-4}$ | $5.6(10)^{14}$ | $7.8(10)^{-2}$ |

[1] Meyer, Kinetische Theorie der Gase, 2d ed., p. 261.

[2] Conduction of Electricity through Gases, 2d ed., p. 43.

for currents of the order of 0.05 ampere in the central portions of the arc. Thermal ionization appears adequate to give such currents at reasonable arc temperatures, provided the effective ionizing potential is about 8.6 volts, but not if the ionizing potential is 16 volts. This value, 8.6 volts, may represent a "radiating" potential of the gas, ionization being a two-stage cumulative effect. Both oxygen and nitrogen have radiating potentials in this region. It is more likely, however, a critical potential of carbon vapor, about which we have no direct experimental evidence.

Of the possible explanations of ionization in this region of the carbon arc, only thermal ionization appears possible. Of course the impact of electrons contributes to the attainment of the necessary high temperatures.

### (c) *Conditions at the Anode.*

No success has attended the effort to obtain explicit quantitative values for the magnitude of the anode drop. It is easy to account for it, however, in a qualitative way. By thermal ionization in the gas, ions are produced at the rate $N/\tau$ per unit volume, $1/\tau$ being the average frequency with which a molecule is thermally ionized. If $t$ is the average life-time of a positive ion, $Nt/\tau = \nu$, where $\nu$ is the number of positive ions per unit volume. Thus $t = \nu\tau/N$ is the average life-time of a positive ion. The average distance which a positive ion moves between formation and recombination is then given by

$$d = uEt = uE\frac{\nu\tau}{N}.$$

Outside the regions of the anode or cathode drops, $\nu$ is given by equation (10) and $u$ by equation (12). Inside the region of the anode drop, $\nu$ has a smaller value than that predicted by equation (10) since the ions are swept away too fast to permit the assumption of equilibrium conditions between production and recombination of ions at a specified point. In any case, the positive ions formed near the anode travel a distance $d$ somewhat greater than that predicted by the above equation before disappearing. It is therefore evident that, if the space charge is zero in the main body of the gas, there must be a deficiency of positive ions within a distance $d$ from the anode. The concentration of positive ions varies from 0 at the surface of the anode to $\nu$ at a distance $d$ from it. Within this distance there exists a negative space charge and the electric intensity rapidly increases with nearness to the anode.

Probably a second factor contributing to the drop at the anode is a space charge, very near its surface, due to the suppressed thermionic emission from it, when it is hot.

Under some conditions, also, positive ions may be produced by electron impact against the anode, or against vapors emitted by the anode when it is heated.

Varying the nature and geometrical relation of the anode to the cathode may vary any or all of the above factors, and thus account for the fact that the anode drop is not a constant in a given type of arc, but appears to be essential only for the reason that the anode must receive the electronic current which leaves the cathode.

## Conclusions.

The arc seems dependent on an adequate supply of electrons at the cathode, whose escape from it is made possible by sufficient ionization of gas near it to form a positive space charge. The calculations which are given support this view and indicate that the thickness of the region of the cathode drop is of the order of the electronic mean free path in the gas.

There is no reason for doubting that any origin of sufficient electronic emission from the cathode would serve to maintain an arc, but these currents appear actually to be of thermionic origin. It seems unlikely that photo-electric emission can be obtained large enough to support an arc, and chemical action or bombardment by positive ions are effective only as they contribute to the general or local high temperature of the cathode.

It is possible that, in certain cases, true thermionic emission may be obtained in larger amount than would be predicted by Richardson's thermionic equation (1). Impacts of positive ions may produce local high temperatures which cannot be allowed for in applying Richardson's equation. Furthermore, in gases at high pressure, the region of the cathode drop may be so thin as to give rise to such a high electric intensity as to draw out of the cathode electrons which would not otherwise be included in the saturation current. In other words, the field may extract electrons from the region of the "electron atmosphere." This would be equivalent to a reduction in the ordinary value of the work function $\phi$ for the material of the cathode, as is at once evident when it is remembered that $\phi$ includes the effect of the attraction of the positive charge induced on the surface of the cathode by the escaping electron. Millikan and Shackelford [1] were unable thus to extract electrons from metals by fields lower than 4,000,000 volts per cm. At the high temperature of an arc cathode, however, the electron atmosphere should extend farther from the cathode surface and an effect of the sort suggested may be appreciable.

[1] Phys. Rev., 15, p. 239, 1920.

We have one bit of positive evidence in some work in this laboratory in which abnormally large thermionic currents were obtained from a hot tungsten filament when the anode was brought very close, perhaps within the region of its electron atmosphere.

A recent paper by Dushman [1] has shown that this effect, first suggested by Schottky, is appreciable in ordinary measurements of thermionic emission. It should be much greater in the case of high pressure arcs.

Finally, it may be mentioned that equation (7) suggests that the ionization should increase as the square of the gas pressure. This is qualitatively in agreement with the observation that the intensity of spectral excitation in an arc increases very rapidly with increase in gas pressure.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY,
September 25, 1922.

[1] Dushman, Rowe and Kidner, Phys. Rev. 21, 207, 1923.

# INTENSITIES IN THE HYDROGEN SPECTRUM.

By A. Ll. Hughes and P. Lowe.

Abstract.

**Variation of the intensity of hydrogen spectrum lines with the energy of the exciting electrons, 29 to 110 volts,** pressure and current being maintained constant, was studied quantitatively by the use of a three-electrode tube in which electrons from a long oxide-coated filament were accelerated through a nearby grid with a field-free space between the grid and the plate. The spectra of light from this space, excited with various accelerating potentials, were photographed on the same plate and the densities of certain lines were measured by a microphotometer. Of the *series lines*, H$\alpha$ shows practically constant density for the whole range of voltage, while H$\beta$, H$\gamma$ and H$\delta$ increase in density at first rapidly and then more slowly, tending to constant values for the higher electron energies. The density change was greater the higher the term number. Of the *lines of the secondary spectrum*, $\lambda\lambda$ 6327, 6225, 6135, 6122, 6030 and 6018 decrease very rapidly in density as the energy of the electrons is increased, while $\lambda\lambda$ 5013, 4934, 4929, 4743, 4632 and 4205 reach maximum density between 30 and 40 volts and then grow weaker but not as fast as the first six lines. Since the series spectrum is associated with the atom and the secondary with the molecule, it is inferred that the *ratio of dissociating to non-dissociating collisions* increases rapidly with the energy of the bombarding electrons between 29 and 110 volts. The change in relative intensity of the series lines suggests that the higher the energy of electron impact the more likely is the electron within the atom to be displaced to the remoter Bohr orbits when the molecule is dissociated.

IT is a matter of common observation that the distribution of intensities in the spectrum of hydrogen varies enormously as the conditions of excitation are changed. Though it is evident that a study of the conditions causing intensity variations might well lead to information on the nature of the origin of the spectrum, quantitative studies of the intensities in the hydrogen spectrum are very few. Merton and Nicholson [1] give an account of some measurements on the changes in distribution of energy among the first four lines of the Balmer series when a condensed discharge is substituted for an uncondensed discharge. The independent variable, however, in this type of work is not a clearly defined quantity. It seemed, therefore, worth while to try and measure the intensities of the hydrogen lines as a function of some definite fundamental variable. The generally accepted theory of radiation is that radiation is given out when the atom (or molecule) has been put into an abnormal state by radiation, or by electron impacts, and is returning to its normal state. If we con-

[1] Phil. Trans. Roy. Soc., A, 217, p. 237, 1917.

fine ourselves to the case when the atom or molecule is radiating as a result of a collision with an electron, then clearly the energy of impact of the electron is the important fundamental quantity governing the emission of radiation. It is, of course, recognized that the resulting effect may be profoundly affected by other factors, *e.g.*, pressure which determines the proximity of the molecules. Nevertheless, it is the impact of the electron which puts the atom into a state in which it can emit radiation and one can imagine a state of affairs (very low pressure, very feeble currents) in which the subsequent factors controlling the radiation become negligible.

The method employed by Fulcher [1] was to accelerate electrons from a hot cathode by a definite potential to an anode. Spectrograms of the light excited by collisions in the intervening space were taken for different accelerating potentials. Fulcher found that, as the velocity of the electrons was decreased, the secondary spectrum (at least many lines belonging to it) was much intensified with respect to the Balmer series. Holtsmark [2] accelerated electrons from a hot cathode to an anode in which there was a suitable opening through which some of the electrons could pass into a space where there was no electric field. He measured the intensities of the four leading Balmer lines radiated from this space, and found that the ratios of the lines $H\alpha$, $H\beta$, $H\gamma$, and $H\delta$ were unchanged as the energies of the electrons were increased from 17 volts to 1,700 volts.

The secondary spectrum is very complicated. Merton and Barratt [3] give a list of over 1,000 lines, in which they indicate the manner in which many of these lines are affected by variations in conditions of excitation. Some lines are relatively intensified at high pressures, some at low pressures, some by a condensed discharge, and some in the presence of helium. Certain lines are designated as "Fulcher Lines," being those observed by Fulcher as intense lines when excited by low velocity electrons. Merton and Barratt were unable to arrive at any comprehensive generalization, but on the whole they found that those lines which were relatively intensified at low pressures were Fulcher lines, while lines which were relatively intensified at high pressures (and generally with a condensed discharge) were not Fulcher lines.

In the present investigation, the authors have measured the intensities of the first four Balmer lines and a number of the more prominent secondary lines. The authors were unaware of the work of Holtsmark until

[1] Astrophysical Jour., 37, p. 60, 1913.
[2] Phys. Zeits., 15, p. 605, 1914.
[3] Phil. Trans., A, 222, p. 369, 1922.

after the investigation was completed; their results are not in agreement with those of Holtsmark.

## Apparatus.

A V-shaped oxide-coated filament, about 20 cms. total length, served as the source of electrons. Parallel and close to the filament was a grid of fine nickel wire. Beyond the grid was a semicircular nickel plate approximately fitting the glass tube. The plate and grid were both connected to the positive end of the battery giving the accelerating voltage, while the other end was connected to the filament. The electrons were quickly accelerated to the grid and then passed into a field-free space with a velocity determined by the accelerating potential. A two-prism photographic spectrometer was lined up so that the axis of the collimator was along the axis of the field-free space between the plate and grid. Thus, we photographed the spectrum produced by the impact of electrons of definite velocity (the pressure being kept sufficiently low to ensure that only a small percentage of electrons made a second collision within the field-free space). Hydrogen was generated from pure zinc and sulphuric acid and passed through phosphorus pentoxide and through charcoal cooled by liquid air, into a reservoir. It was passed into the apparatus through a fine capillary glass tube, the pumps being in action continuously. In this way, a stream of hydrogen was passed through the apparatus, the pressure remaining very constant. U-tubes on the inlet and outlet sides of the experimental tube were cooled by liquid air.

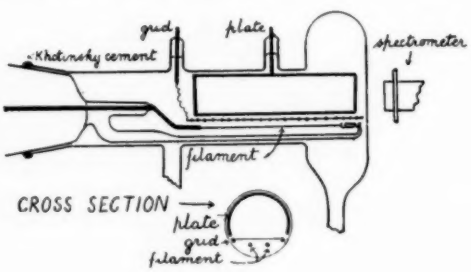


Fig. 1.

Panchromatic plates were used so as to photograph the whole spectrum. Many photographs were taken to find out the best conditions. The final plates, giving the results recorded in this paper, were taken under as constant conditions as possible. Ninety minutes' exposure was given for each spectrogram on the first two plates, the pressure and the current through the field-free space being kept constant. On the first plate exposures were made with 110, 85, 50 and 35 volts accelerating potential. On the second plate exposures were made with 110 volts (to link up with

the first plate), 65, 40 and 34 volts. On the third plate there were two exposures of four hours each corresponding to 29 and 35 volts. The electron current for the first two plates was 50 milliamperes and the pressure was .050 mm. For the third plate the current was 5 milliamperes and the pressure .072 mm.

The "opacities" of the lines on the photographic plate were measured by a microphotometer.[1] The results are given in "densities," the relation between density $D$ and opacity $O$ being given by

$$D = \log_{10} O.$$

Unfortunately we had no means of calibrating our plates so as to deduce the intensity of the radiation in any line from the opacity of the line on the plate. However, it is well known [2] that the density is proportional to the logarithm of the exposure or, when the time of the exposure is unchanged, to the logarithm of the intensity, except when the density is very great or very small in which case a small change in density indicates a greater change in intensity than over the straight portion of the curve. So far as our measurements are concerned, only lines of small densities are likely to be affected in this sense. We have left our results in densities.

## Results.

Fig. 2 gives the curves connecting the densities of the Balmer lines with the voltage accelerating the electrons.

As Fig. 2 shows, the values for 110 volts on both plates are (except for $H_\gamma$) practically identical, indicating that, so far as the 110-volt exposures go, the plates are fairly comparable. Unfortunately there is an appreciable difference in shapes of the curves for the two plates. However, the difference between them does not affect the conclusions drawn. The spectrograms obtained in the standard time, $1\frac{1}{2}$ hours, for voltages below 34 volts were so weak that it was necessary to give much longer exposures. Hence spectrograms for 29 and 35 volts were taken on plate 3, the exposures lasting 4 hours. As higher current could not be obtained at 29 volts, current was maintained in both cases at 5 milliamperes and to get more light the pressure was increased a little to .072 mm.

[1] We are indebted to Dr. Foote, of the Bureau of Standards, for the design of an improved form of microphotometer. The method of using it is sufficiently described in "A New Microphotometer," Bur. Stand., Sci. Papers, No. 385, 1920, by Drs. Meggers and Foote.

[2] See Davis and Walters, "Sensitometry of Photographic Plates," Bur. Standards, Sci. Papers, No. 439, 1922.

To link the 29-volt spectrogram on plate 3 with those on plate 1, we measured the difference between the densities of the lines for 35 volts in plate 1 and the corresponding densities in plate 3, and added this difference to the 29-volt densities in plate 3. This method may be open to criticism. Its validity implies that the density is proportional to the logarithm of the exposure. It would have been more satisfactory of course to get the 29-volt spectrogram under exactly the same conditions as the others, but this was not practicable.

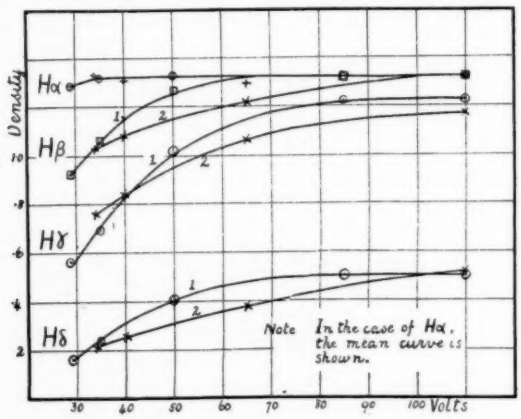


Fig. 2.

*The Balmer Lines.*—$H_\alpha$ remains practically unchanged in density from 30 to 110 volts. $H_\beta$, $H_\gamma$, and $H_\delta$ increase in density as the voltage increases and tend to reach a constant value as the voltage approaches 110 volts. Between 29 and 110 volts $H_\beta$ changes in density by .41, $H_\gamma$ changes by .62, while $H_\delta$ changes by only .34. It was mentioned earlier that when densities are *small*, a given change of density corresponds to a much larger change in the logarithm of the intensity than it does on the straight portion of the characteristic curve for the plate. Hence the density change for $H_\delta$ may, in reality, mean a greater relative change in its intensity as the voltage is increased from 29 to 110 volts than for $H_\gamma$. If this is the case, and it seems most probable from other data, we could generalize the results and say that, as the energy of impact decreases from 110 volts to 29 volts, the distribution of energy among the Balmer lines is at first practically constant and then alters more and more rapidly as the voltage is decreased. The alteration is such that the intensity of the $H_\alpha$ line remains almost unchanged over the whole range, while the intensities of the other lines decrease, the amount being greater, the higher the term number of the line.

*The Secondary Spectrum.*—In selecting twelve prominent secondary lines for measurement, we first of all tried to choose lines about which there could be no confusion as to identity on our plates and then, among

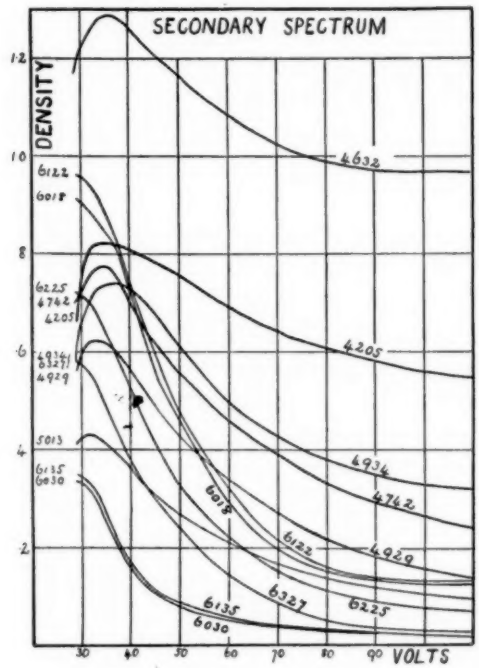


Fig. 3.

these, we chose lines which represented the various classes indicated by Merton and Barratt.[1]

To present the results for these secondary lines in the same way as for the Balmer lines would require twenty-four curves. To avoid unnecessary confusion, a mean curve was drawn for each line from the densities on the three plates and only such mean curves are shown. (The curves are of course not so smooth as the absence of marked points may imply.)

The curves fall into two classes. λ 6327, λ 6225, λ 6135, λ 6122, λ 6030 and λ 6018 have no maximum, and their intensities (as inferred from their densities) fall off exceedingly rapidly as the accelerating voltage is increased. (Earlier remarks on the interpretation of very small densities should be remembered if doubts arise as to the applicability of this statement to the weaker lines λ 6135 and λ 6030.) The lines in the other class, λ 5013, λ 4934, λ 4929, λ 4632, λ 4743, and λ 4205, have a maximum density between 30 and 40 volts, and their densities do not

[1] Loc. cit.

fall off so rapidly with increasing voltage. This division falls in fairly well with Merton and Barratt's classification.

Of the lines in our first class, λ 6327, λ 6225, λ 6122, and λ 6018 are classified by Merton and Barratt as "low pressure" lines and as Fulcher lines. λ 6030 may be a mixture of λ 6032 and λ 6028, the former being a "low pressure" and a Fulcher line. The remaining line λ 6135 seems to be an exception, for they record it merely as a "high pressure" line. However this must be a mistake for Fulcher records it as one of the main band lines.

In our second class, we have no lines which Merton and Barratt designate as Fulcher lines. Only one line, λ 4743, is a "low pressure" line. This is probably a fusion of λ 4743.4 and λ 4742.7, the former of which is classed as a "low pressure" line, while the latter is not characterized in any way. The other lines are apparently indifferent to pressure as Merton and Barratt do not list them either as high or low pressure lines. Three of them, λ 4934, λ 4929, and λ 4632, are noted as lines which show the Zeeman effect. (Apparently no Fulcher line shows the Zeeman effect).

## Discussion.

The possible results of a collision between an electron and a hydrogen molecule are given in Table I.

Table I.

| | | Min. Energy Required. |
|---|---|---|
| No dissociation: | (1) Ionized molecule..... | ? |
| | (2) Partially ionized molecule[1]..... | ? |
| Dissociation: | (3) Neutral atom and partially ionized atom..... | $3.5 + 10.2 = 13.7$ volts. |
| | (4) Neutral atom and ionized atom. | $3.5 + 13.5 = 17.0$ volts. |
| | (5) Two partially ionized atoms.... | $3.5 + 2 \times 10.2 = 23.4$ volts. |
| | (6) Ionized atom and partially ionized atom..... | $3.5 + 10.2 + 13.5 = 27.2$ volts. |
| | (7) Two ionized atoms..... | $3.5 + 2 \times 13.5 = 30.5$ volts. |

If, as is generally believed, the secondary spectrum is due to the molecule and the series spectrum to the atom, then the results plotted in Figs. 2 and 3 would indicate that the higher the energy of the impacting

[1] By ionized molecule or atom is meant one from which an electron has been removed completely, leaving the residue positively charged. There seems to be no generally accepted terminology for the case of a molecule or atom in which the electron is removed to one of the outer Bohr orbits, the atom remaining neutral. Such atoms are often called "abnormal," but the verb "abnormalize" is too unattractive for use. "Partial ionization" is used here.

In the third column, the theoretical minimum energies required for each type of dissociating collision are calculated from Bohr's theory and the energy required for dissociation. The calculation refers only to the type of partially ionized atom in which the electron is moved to the second Bohr orbit. Removal to the 3d, 4th, . . . orbits of course gives other types of partially ionized atoms.

electron, the greater the ratio of the dissociating collisions to the non-dissociating collisions.

*The Series Spectrum.*—The atoms may return to their normal state giving out the series spectrum after having been ionized (or partially ionized) in one of two very distinct ways. One way is that contemplated in (3) to (7) of the above list. The other is that which results from an electron colliding with a *free* atom.

Free atoms however only exist under conditions where the discharge is so intense that atoms, once dissociated, can be struck again by electrons before recombining to form molecules. (Conditions of this kind predominate in some of Professor R. W. Wood's experiments on the production of the series spectrum.) The density of the electron current is, in our own experiments, probably much too low to allow impacts between electrons and atoms to be other than a negligible fraction of the total number of impacts. Hence we believe that the Balmer lines in our investigation must be attributed to impacts of types (3) to (7) in the list. If every dissociating collision resulted in completely ionized atoms (or a constant proportion of neutral and completely ionized atoms), then the radiation would be conditioned by the atom capturing a free electron. Hence the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ would have nothing to do with the energy of the electrons producing the dissociation and would therefore be constant, and the intensities (being supposedly proportional to the number of radiating units) should vary with the potential in the same way as the dissociation. One of the authors [1] found that dissociation of hydrogen began when the energy of the impacting electrons was about 13 volts and increased, very rapidly at first, until it became practically constant above about 50 volts. Since we find that the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ are not constant, and since their intensity changes do not run parallel with the amount of dissociation, the supposition cannot be true. It is therefore very likely that a large part of the dissociating collisions result in partially ionized atoms, in which the electrons are shifted to the outer orbits. The rapid changes in the ratios $H_\alpha : H_\beta : H_\gamma : \cdots$ at low voltages suggest very strongly that the higher the energy of the impacting electrons, the greater the proportion of partially ionized atoms in which the electron is shifted to orbits remote from the center. The approximate constancy of the ratios at the higher voltages need not be taken as proof that all the dissociating collisions here are now of the kind resulting in completely ionized atoms, as it may happen that the ratios of the different types of partially ionized atoms tend to a constant value at the higher voltages. What seems certain is that, especially

[1] Hughes, Phil. Mag., 41, p. 778, 1921.

at the lower voltages, dissociation into partially ionized atoms predominates. The approximate constancy of the $H_\alpha$ line would suggest that the number of atoms in which the electron is shifted to orbit 3 (since $H_\alpha$ is represented by $N(1/2^2 - 1/3^2)$) is nearly constant from 29 up to 110 volts. (It would be interesting to see whether this held between 29 and 13 volts.)

*The Secondary Spectrum.*—It would be natural to infer that our six lines between λ 6000 and λ 7000, which behave in the same way, originate in the same type of ionization of the molecule (whether complete or partial) and that our other six lines are to be attributed to some other type of ionization. It is exceedingly difficult to draw any useful conclusions in the absence of a satisfactory theory of the secondary spectrum. Merton and Barratt (loc. cit.) give seven different criteria for classifying the lines in the secondary spectrum, and state that many exceptions exist to any general correlation which can be laid down. It does not seem at the present moment profitable to speculate further on the origin of the various types of the secondary spectrum.

As suggested earlier in the paper, the purpose underlying this paper was to find out the variation in the distribution of energy in the hydrogen spectrum when the only variable was the energy of impact. As the effect of pressure on the distribution would be expected to diminish as it was reduced, the ideal way of conducting the experiments would be to work at very low pressures. Unfortunately, the amount of radiation given out at pressures below about .02 mm was so little with our arrangements that it would require extremely long exposures (which in turn would increase the difficulty of keeping other conditions constant) to get satisfactory spectrograms.

Preliminary experiments have been made on the effect of pressure. We plan to continue the investigation especially in the region of low voltages where the changes are most rapid, for hydrogen and other gases. In this region an equipotential source of electrons will add precision. Many investigators have worked with apparatus of this type on the critical potentials associated with the initiation of radiation (*e.g.*, the large body of work on radiating potentials), but practically nothing has been done on the quantitative distribution of radiation above these critical potentials.

The microphotometer was purchased by means of a grant from the Honorary Advisory Council for Scientific and Industrial Research of Canada.

QUEEN'S UNIVERSITY,
Kingston, Ontario,
October 21, 1922.

# THE PENETRATION OF CATHODE RAYS IN MOLYBDENUM.

By D. L. Webster and A. E. Hennings.

Abstract.

**Penetration of cathode rays into a target.**—(1) *X-ray spectrum method.* The farther a ray penetrates into the target the more the x-rays excited by it are absorbed by the target material before coming out. X-rays just harder than the $K$ absorption limit are absorbed more strongly than those just softer. If the intensity of the spectrum emitted, except for the characteristics, is a continuous function of the wave-length and if the discontinuity in absorption coefficient is $\mu_K$ and the observed ratio of intensities on each side of the discontinuity is $R$, then the logarithmic mean depth of penetration $\bar{x} = \mu_K^{-1} \log R^{-1}$, for voltages above the minimum necessary to excite radiation of the absorption limit frequency, 20 kv. in case of Mo. (2) *Results for molybdenum.* To reduce the effect of stray x-rays, a calcite crystal was used and narrow slits which limited the incident beam to 8′ 30″. The voltages needed to make the mean depth of excitation of this frequency equal to 1, 2 and 3 $\mu$ were found to be about 24, 44 and 67 kv. respectively. The increased difficulty of penetration beyond the first micron is probably due to the deflection of the cathode rays by the atoms.

**Definite time exposure method of measuring ionization currents.**—Instead of using a stop-watch to measure the time for a given deflection, an instrument was devised which would open the lead shutter in front of the ionization chamber for a definite time interval, from 1 to 120 seconds, with great accuracy. This instrument contained a ratchet wheel driven by an escapement actuated by current impulses from a master clock.

## I. The Problem.

THE penetration of cathode rays in matter is important for three reasons:

First, it gives evidence on the forces acting on an electron that comes near an atom.

Second, the penetration of cathode rays in a metal is important in x-ray experiments, because the x-rays will be produced below the surface, and will be absorbed by the material of the target, in getting out, to an extent depending on the depth of their production and the frequency of the rays considered. This makes a correction to be applied to all x-ray measurements before they can be used for any accurate theoretical work.

Third, since each cathode ray goes through many atoms before stopping, the intensity of the x-rays depends on this number of atoms; or conversely, the point of greatest theoretical interest is not the whole intensity, but the intensity per atom penetrated at any given speed.

For the first point, on electronic forces, and the third, on intensity

reduction, we need data on the length of an electron's path, the number of atoms per unit length, and the deflection and loss of speed per unit length. For the length of path and its deflections, the most obvious method is by stereoscopic photographs with C. T. R. Wilson's apparatus for visible electron tracks. For the loss of speed, this should be combined with measurements of speeds after passing through very thin films, such as were first made by Whiddington, but they should be extended to other speeds than the maxima in the emerging rays, and combined with deflection measurements.

Such a set of measurements, when complete, could be used to calculate x-ray absorptions in the target as well. But for that purpose alone, we can fortunately get some fair approximations, with less extensive data, by measuring the absorption of the emerging rays directly. At the same time, calculating back from these absorptions, we can get some rough data on the average depths reached by the cathode rays. It is this type of measurement, applied to molybdenum, that forms the object of the present paper.

## II. History.

The first measurement of the mean depth of production of x-rays was that of W. R. Ham.[1] His work, in 1910, was necessarily done with unresolved x-rays, due to cathode rays of variable voltage, and depended on measurements of the relative strengths of x-rays coming out at different angles to the target surface, but with all other conditions the same. W. P. Davey,[2] in 1911, used the same apparatus, and L. G. Davey[3] used a modification of the same method. Ham found the depth in a lead target to change from 0.42 to 0.64 micron while the potential changed from 14 to 21.3 kv. W. P. Davey found for silver 0.54 to 0.92 micron at 10 to 17 kv.; and L. G. Davey, with a platinum target, got 2.0 microns at 43 kv.

J. J. Thomson[4] had previously worked out a theory, which made no attempt at more than a rough approximation, but led to the result that the speed of a cathode ray, starting at $v_0$, would be reduced in a distance $x$ to $v_x$, where

$$v_x^4 = v_0^4 - ax,$$

$a$ being an undetermined constant.

Whiddington[5] tested this law with thin films of gold and aluminum,

[1] W. R. Ham, Phys. Rev., *30*, 1, Jan., 1910.
[2] W. P. Davey, J. Franklin Inst., March, 1911.
[3] L. G. Davey, Phys. Rev., *4*, 217, Sept., 1914.
[4] J. J. Thomson, Conduction of Electricity through Gases, 2d ed., p. 378.
[5] R. Whiddington, Proc. Roy. Soc., A*86*, 360, Apr., 1912.

in leaf form, and an arrangement of magnetic fields for measuring his speeds. He found the cathode rays emerging from the leaf to be rather heterogeneous in speed, and measured only the fastest, on the theory that these were the ones that had come through straight, while the others had been deflected and perhaps returned to their original direction, thus having larger values of $x$. In this way he deduced the values

$$a_{Al} = 732 \times 10^{40} \frac{\text{cm.}^3}{\text{sec.}^4}$$

and

$$a_{Au} = 2540 \times 10^{40} \frac{\text{cm.}^3}{\text{sec.}^4}.$$

Expressing the equation in equivalent potentials, we have

$$V_x^2 = V_0^2 - bx,$$

with values

$$b_{Al} = 0.585 \times 10^6 \frac{\text{kv.}^2}{\text{cm.}}$$

and

$$b_{Au} = 2.03 \times 10^6 \frac{\text{kv.}^2}{\text{cm.}}.$$

From this, setting $V_x = 0$, we should calculate maximum depths for gold, at 21.3 kv., 2.24 microns, and at 43, 9.1, which are about four times the mean values for lead and platinum found by Ham and Davey respectively.

A part of this difference is doubtless explainable by the fact that Whiddington's law gives maximum depths, while the others give weighted means. Balancing off the greater x-ray efficiency at higher speeds against the greater penetrating power, one might reasonably expect this weighted mean to be about half the maximum depth. To reduce the mean to a quarter, there must be some other factor, which one may guess from C. T. R. Wilson's experiment to be the deflection of the cathode rays into erratic paths. Whether or not this is the reason, it is at least evident that the practice of using Whiddington's data directly, for the calculation of target absorption, is open to serious question, and more exact data are needed.

## III. The Present Method.

From Whiddington's data, one would expect a great discontinuity at the $K$ absorption limit of the emitting substance, because rays of a slightly shorter wave-length are absorbed several times as much as those slightly longer. Such a discontinuity fails to appear in most cases. It was indeed found by one of us in some spectra[1] of rhodium, but since these

[1] D. L. Webster, Phys. Rev. *6*, 599, June, 1916.

were obtained with rays emerging at a very small angle from the target surface, and the surface was quite visibly rough, it could not be interpreted as evidence of noticeable penetration. On the other hand, if one were to apply Kirchhoff's law to x-rays, one might expect a discontinuity in the other direction, the intensity of the shorter wave-lengths being the greater, by a factor of about 6.5 in rhodium or molybdenum. This difference might of course be cancelled by absorption in some cases, but with the variety of conditions used, the absorption certainly could not always be of exactly the right amount. Since x-rays are not a temperature effect, however, this application of Kirchhoff's laws is mere guesswork, and the absence of any very noticeable discontinuity is good evidence for the belief, which will be adopted here as a fundamental postulate, that *the continuous spectrum is produced by a mechanism independent of the characteristic.*

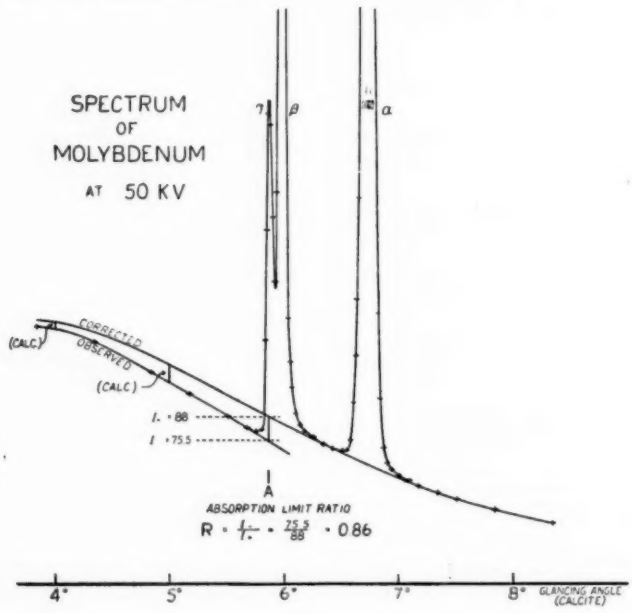


Fig. 1.

Molybdenum spectrum at 50 kv., illustrating discontinuity at $K$ absorption limit.

The $K$ characteristic is almost surely produced by the removal of electrons from the $K$ positions in the atoms and their replacement by other electrons from the $L$, $M$, etc. On the other hand, in the higher frequencies of the continuous spectrum the quanta are greater than can be obtained by replacing even these inner electrons from anywhere else. Therefore it would be unreasonable to assume that these quanta

could be obtained any more readily from the $K$ electrons than from any others, and the independence of the continuous and characteristic spectra would be predicted theoretically.

The present method is therefore to make a more careful search for a discontinuity in the observed spectrum, and to interpret it as due entirely to absorption, and then to try to separate the parts due to absorption by surface irregularities and to true penetration. A typical spectrum, illustrating the method, is shown in Fig. 1.

## IV. The D.C. Generating Plant.

The potential for the tube was obtained from a D.C. outfit patterned in general after that of A. W. Hull, but modified so as to make use of both voltage waves, one in one condenser and the other in another, as shown in Fig. 2. This makes the potential of the D.C. line practically twice

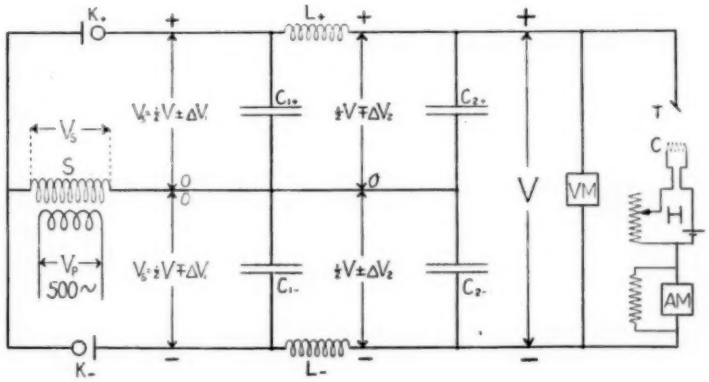


Fig. 2.

Essential features of high potential D.C. outfit. $S$, secondary of 500-cycle transformer; $K_+$, $K_-$, kenotrons; $C_{1+}$, $C_{1-}$, $C_{2+}$, $C_{2-}$, condensers; $L_+$, $L_-$, choke coils; $VM$, voltmeter; $AM$, milliammeter; $H$, cathode heating circuit; $C$, cathode; $T$, target. Potentials denoted by $V$'s with appropriate subscripts.

the peak voltage of the transformer. It also puts the 500-cycle fluctuations in such a phase relation that, if the two sides are symmetrical, their effects on the potential difference between the + and − lines must cancel. Only the first harmonic is then appreciable. If any point of such an outfit is to be grounded, it should be the middle line, because if either the positive or negative is grounded, the distributed capacitance of the transformer is liable to introduce fluctuations. It is not, however, necessary to ground any point, as the essential function of the middle line is to connect the transformer to the condensers.

The voltage fluctuation, $\Delta V_2$, on the second condenser, of the primary

A.C. frequency, is not exactly calculable, but can readily be shown to lie between 1 and 2 times

$$\Delta V_2 = \frac{\pi i}{C_1 C_2 L \omega^3},$$

where in this apparatus $C_1$ (either $C_{1+}$ or $C_{1-}$) $= 2.8 \times 10^{-3}$ mfd., $C_2 = 5.6 \times 10^{-3}$ mfd., $L = 12{,}000$ henries, and $\omega = 480 \times 2\pi$ sec$^{-1}$. This makes it 1 or 2 times 0.4 volt per milliampere of tube current, which is quite negligible.

The only appreciable fluctuations in voltage were those due to changes of speed of the generator, which were always slow enough to show on the voltmeter and enable us to discard readings where they were greater than normal. Errors in voltage would normally be less than 1/10 per cent., although they might produce much larger changes than that in the x-ray intensities at wave-lengths near the short-wave limit.

The high tension voltmeter was of an electrostatic type previously described by one of us,[1] and was calibrated by current through a 6-megohm resistance.

The milliammeter was a Weston, model 1. It was enclosed, along with its shunt and the whole filament heating system, in a wire cage connected to the high potential source, back of the milliammeter. This precaution is needed at high voltages, even with the best practicable insulation, to prevent errors in the current measurement, due to leakage.

## V. A Device for Timing Ionization Currents Accurately.

The x-ray spectrometer was of the Bragg type, with a quadrant electrometer, mounted above the crystal. It needs no special description, except for one point which we found a great convenience, as well as an improvement in accuracy, by the elimination of the stop-watch usually used in ionization work.

Instead of timing the motion of the electrometer, from the instant the grounding key was lifted, to some other point, we used a lead shutter, placed in the path of the x-rays before they reached the crystal, and opened or closed by an electric current from a clock. The grounding key would first be lifted and the zero of the electrometer scale set on the spot of light from the electrometer. Then the shutter would be opened, kept open for a definite number of seconds, and closed. The electrometer would swing during this time and come to rest momentarily at a certain definite time after the shutter was closed. The time of the exposure, as we may call it by analogy to photography, was always kept the same for all readings on any one spectrum or isochromat, and there-

[1] D. L. Webster, loc. cit.

fore the time of swing after the end of the exposure, and the fraction by which the reading increased in this time, was constant. The resulting reading was therefore proportional to the intensity of the rays. This proportionality, which one might predict theoretically, was checked by tests with different tube currents at the same voltage and frequency.

For timing the exposures accurately, we used current impulses from a good pendulum clock, with a secondary clock, driven by the first, to select the impulses to be used. This selector clock was a single ratchet wheel driven by an escapement, which in turn was driven by a bell magnet with current from the master clock. On the wheel were two pins, so placed as to make contact with a brush at the release of the magnet, and therefore to have the contact already made before the arrival of the next current impulse, that worked the shutter. This arrangement is most important, because it makes the accuracy of the timing depend on the master clock, and not on the selector. By placing the pins in different holes on the wheel, we could use different exposures, varying from 1 second, in runs with strong rays, to 120 seconds with weak. In no case could any error be found, due to any inaccuracy in the exposure, even with the 1-second intervals, which would have been wholly worthless if taken with a stop-watch.

## VI. The Crystal.

For this problem, it is especially important to get accurate data at wave-lengths near the absorption limit, and to avoid as far as possible any influence of stray x-rays belonging to the $K$ series lines. This means, first, the use of fairly narrow slits.

Theoretically, we should expect x-ray emission lines to be very narrow. The Doppler effect due to atomic motion is quite negligible, and Jauncey [1] has shown that the width due to damping by loss of energy should be only $1.2 \times 10^{-4}$ Å. at any wave-length, if the damping follows the classical theory. This width means about 4 seconds of arc as reflected from calcite. Compton,[2] however, finds experimentally in the tungsten $L$ series, widths of the order of 18′ of arc with either calcite or rock salt. Most of this width he explains as due to slit width and imperfections of the crystal with a small addition for complexity of the lines.

In the present experiments the beam was limited by two slits, between the tube and the crystal, of such widths as to give the beam a maximum angular width of 8′ 30″. If the crystal were perfect, and the rays homogeneous, this should represent practically the whole width of each

[1] G. E. M. Jauncey, Phys. Rev., *19*, 64, Jan., 1922.
[2] A. H. Compton, Phys. Rev., *19*, 68, Jan., 1922.

spectrum line. Practically, however, the spectrum lines are all widened at the base, as shown in Fig. 1, above, by stray rays whose intensity is very low compared to that in the centers of the lines, but not negligible compared to the continuous spectrum. With no slit beyond the crystal, except the thin aluminum window of the ionization chamber, which subtends about a degree, this widening at the base is so great as to overlap from the $\alpha$ lines to the $\beta$, and to make an accurate estimate of the intensity between the lines impossible. This is true either with a perfectly clear polished piece of calcite, a clear piece split and not polished, or one split and ground to remove the step-like layers on the surface. Presumably all these crystals must contain many very minute pieces, slightly out of line with the general shape of the crystal, and reflecting some rays at slightly wrong positions.

With a third slit, just in front of the ionization chamber, subtending an angle of about 25′ from the crystal, and just wide enough to be sure to include the whole reflected beam from a true surface, the stray rays were greatly reduced, and it became possible to measure the continuous spectrum, as in Fig. 1, with much less error from this cause. It must be remembered, however, that some error from stray line radiation is still present, and that it always acts to make the estimated discontinuities and depths of cathode ray penetration too large.

## VI. Results.

Plotting spectra at various potentials, with no measurements at angles reflecting the characteristic lines, we get a set of graphs of which typical examples are given in Fig. 3. The discontinuity is not easy to estimate accurately, especially at the lower voltages, because of the extrapolations needed to get to the absorption limit, and the probable error in the ratio $R$, of intensity on the long wave side to that on the short, is about 1 or 2 per cent.

The method of extrapolation, illustrated by the graphs labeled as "calculated," is as follows: First, extrapolate by guess, and estimate the value of the ratio $R$; second, from this "1st $R$," calculate the losses of intensity by the $K$ absorption at some shorter wave-lengths (shown on each graph by vertical lines); third, plot the intensities corrected for $K$ absorption at these wave-lengths, and see if they form a smooth continuation of the graph on the long wave side. If they do, the "1st $R$" can be accepted as a final value. If not, a second trial value of $R$ is taken, and the process repeated, until a smooth curve is obtained. In a few cases, where the primary voltage had been very unsteady and the data were ragged, no smooth curve could be drawn, and such cases were discarded.

In this calculation for the shorter wave-lengths, the change of absorption coefficient was allowed for, and the mean depth of production of such rays was assumed to follow a law like that of the limit frequency, but on a different scale of potentials. Fortunately this assumption did not have to be accurate, so far as the final values of $R$ were concerned.

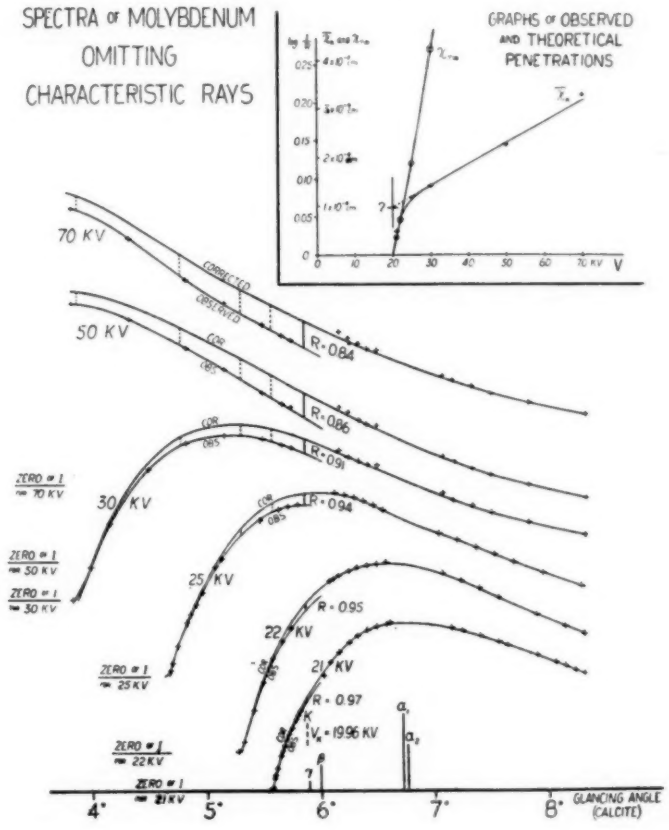


Fig. 3.

Spectra of molybdenum at various potentials with different intensity scales, adjusted for approximate agreement at the $K$ limit; also graph of mean depth, $\bar{x}_K$, calculated from the $K$ limit, and maximum depth $x_{TW}$, calculated from the Thomson-Whiddington law.

To find the mean depth, measured along the line of the cathode rays, we must note that the target was tipped at 45° to the axis of the tube, and the cathode rays, allowing for electrostatic deflection by the field near the target, struck it at some direction probably between 50 and 60° to its surface. The x-rays were taken out through a thin glass window, blown into the tube, at about 80° from the cathode end of the tube axis.

This made an angle between the x-rays and the target surface of about 55°, or practically the same angle for both cathode rays and x-rays. Therefore we shall take the depths along the line of the cathode rays to be the same as on that of the x-rays.

Let $\mu_{L'}$ stand for the absorption coefficient due to the $L$, $M$, $N \cdots$ electrons alone, $\mu_K$ that due to the $K$ electrons, $\bar{x}_K$ the weighted mean depth of production of the $K$ limit frequency, $I_K$ the unabsorbed intensity at the absorption limit $\lambda_K$, $I_+$ the intensity at wave-lengths just above the limit and $I_-$ just below. Then, if the mean $\bar{x}_K$ is weighted logarithmically,

$$I_+ = I_K e^{-\mu_{L'} \bar{x}_K}$$

and

$$I_- = I_K e^{-(\mu_{L'} + \mu_K)\bar{x}_K}.$$

From this we find

$$\mu_K \bar{x}_K = \log \frac{I_+}{I_-} = \log \frac{1}{R}.$$

$\mu_K$ can be calculated from Richtmyer's[1] data, as 639 cm.$^{-1}$.

The graph in the upper right hand corner of Fig. 3 is taken by these formulas from the averages of a few determinations from different sets of data for each voltage, weighted 1, 2 or 3 according to the general appearance or the steadiness of the primary voltage in each case. The spectra at 21 and 22 kv. are weighted low, not because of any unsteadiness, but because the strong curvature of the graphs made extrapolation difficult and the results correspondingly uncertain. The values of $R$ are given in Table I.

TABLE I.

| $V$. | Weight. | $R$. | Mean $R$. | Mean log 1/$R$. | $\bar{x}_K$. |
|---|---|---|---|---|---|
| 21 kv..... | 1 | 0.97 | | | |
| " ..... | 2 | 0.97 | 0.97 | 0.0305 | 0.5 micron |
| 22 ..... | 2 | 0.95 | | | |
| " ..... | 2 | 0.955 | 0.953 | 0.048 | 0.75 |
| 25 ..... | 1 | 0.925 | | | |
| " ..... | 3 | 0.94 | | | |
| " ..... | 3 | 0.915 | 0.927 | 0.076 | 1.2 |
| 30 ..... | 3 | 0.91 | | | |
| " ..... | 1 | 0.92 | | | |
| " ..... | 1 | 0.925 | | | |
| " ..... | 3 | 0.91 | 0.913 | 0.091 | 1.4 |
| 50 ..... | 3 | 0.86 | | | |
| " ..... | 1 | 0.89 | | | |
| " ..... | 3 | 0.86 | 0.865 | 0.145 | 2.3 |
| 70 ..... | 3 | 0.84 | | | |
| " ..... | 2 | 0.79 | | | |
| " ..... | 3 | 0.805 | 0.81 | 0.21 | 3.3 |

[1] F. K. Richtmyer, PHYS. REV., *18*, 13, July, 1921.

## VII. Conclusions.

It is difficult to compare these data accurately with those of previous observers, whose measurements were on different quantities and with different metals. The nearest to these are those of W. P. Davey, who found mean depths of 0.54 to 0.92 micron for silver at 10 to 17 kv., using x-rays of all frequencies together. His values are of the same order of magnitude as the present ones.

Whiddington's maximum penetrations, for aluminum and gold, may be used by interpolation to give rough values for molybdenum. For this metal we have taken as a rough guess,

$$b = 1.2 \times 10^6 \frac{\text{kv.}^2}{\text{cm.}},$$

and have plotted the predicted maximum depths of excitation of this frequency against the values of $V$, as the graph $x_{TW}$. The curve agrees well with that of $\bar{x}_K$ at first, but keeps on rising more and more rapidly, while $\bar{x}_K$ rises only very slowly beyond 25 kv. At 70 kv., $x_{TW} = 37$ microns, more than 11 times the observed depth, $\bar{x}_K$.

This rapid change in the behavior of $\bar{x}_K$ needs explanation. The data at 21 and 22 kv. are very hard to get accurately, and no great confidence can be placed in them, because of the weakness of the rays at those voltages and the curvature of the spectrum graphs in the region extrapolated. At first, before special efforts were made to get these points, it was supposed that there must be a constant absorption by irregular humps on the target about one micron high, as indicated by the intercept marked "?" on the small diagram of Fig. 3. With a smooth surface, such as the target was, it did not seem reasonable to expect such large humps, yet it was not certain that they did not exist. The later data, however, including all those of Fig. 2, were taken with a perfect mirror surface, made by melting the focal spot with 5 times the normal current, and then cutting off the potential while it cooled. No humps could be expected here as large as half a wave-length of light, and certainly not a whole micron. We must therefore eliminate any allowance for surface absorption, and conclude that Fig. 2 gives a fair approximation to the true penetration law.

The explanation is presumably that the cathode rays go in approximately like Whiddington's straightest rays for the first micron or so, but by that time get so badly thrown out of line that higher voltages accomplish very little in further penetration. This conclusion is in accord with the known tortuous character of C. T. R. Wilson's electron tracks.

Stanford University,
California,
August 29, 1922.

# X-RAY ISOCHROMATS OF MOLYBDENUM.

By D. L. Webster and A. E. Hennings.

Abstract.

**Variation of intensity of x-radiation from molybdenum with voltage, for wave-lengths 0.246 to 123 A.**—The ordinary x-ray spectrum, intensity as function of wave-length, cannot be interpreted in terms of energy because of the unknown variation of several factors with frequency. In the case of isochromats, intensity per cathode ray for a given wave-length as function of voltage, the problem is simpler. *Measurements up to twice the quantum voltage* were made in each case except where that would exceed 70 kv. and both voltage and current were determined to 1/10 per cent. The angle between the x-rays and the beam of cathode rays was about 110°. To avoid correcting for the variation of size of focal spot, a single narrow slit was used near the crystal. The correction for crystal scattering was determined from measurements on each side of the reflected beam; it was less than one per cent. except near the quantum voltage. *The correction for target absorption* was taken to be $\mu\bar{x}$ where $\bar{x}$, the mean depth of penetration, was computed from the data reported in the preceding article. After making these corrections, the isochromats were found to be straight lines except for some downward concavity near the feet. The results for 0.41 to 1.23 Å agree within 1 or 2 per cent with an *empirical equation for isochromats* which is given. The values for the shorter wave-lengths are too unreliable at high voltages to serve as tests. From the above equation, an expression for the *radiation from a vanishingly thin target* is derived which involves $b$ the coefficient of the Thomson-Whiddington law. If this law and the $V^2$ law for total intensity are correct, the *probability of emission of a quantum* with frequency between $\nu$ and $\nu + d\nu$ in distance $ds$ is $ids d\nu/h\nu$, where $ids d\nu$ is the intensity per cathode ray, with the thin target.

## I. The Problem.

An x-ray spectrum, as ordinarily plotted, is a graph of ionization against wave-length or glancing angle. To interpret it in terms of energy, we must know several factors, such as the efficiency of reflection of the crystal and the energy value of the ionization unit, all of which vary from one wave-length to another, in ways that are at present unknown. In an isochromat, or graph of intensity against potential for a single frequency, most of these unknown functions of the frequency can be confined to a factor that, while still unknown, is at least constant for any one isochromat. Consequently, the form of the isochromat can be determined, except for a constant factor, much more readily than that of a spectrum.

There are, however, two factors that are variable even here. One is

the diffuse scattering of x-rays by the crystal, that results in a slight impurity in the spectrum, like the stray light in an optical spectrometer. The other is the absorption of some of the rays in getting out of the target, that depends on the depth at which they are excited, and consequently on the potential driving the cathode rays. Both factors produce only small errors, often negligible in a first approximation, but important when an accuracy of one per cent. or so is desired.

The purpose of the present paper is to take a set of data, correcting for these factors, on the rays most convenient for this purpose, and to see what such results signify about the mechanism of electron collisions and radiation. For a brief account of the history of this problem, the reader is referred to the Report of the X-ray Committee of the National Research Council.[1]

## II. Apparatus.

The apparatus used here was that of the preceding paper, and needs no further discussion, except to emphasize two points: First is the accuracy of the calibration of the high tension D.C. voltmeter, which was not especially important there. The 6-megohm resistance used in calibrating it was measured with apparatus standardized by a set of new 10,000-, 1,000- and 100-ohm coils, certified by the Bureau of Standards. The current through it was measured by the potential drop it produced in the 100-ohm standard inserted in the middle of the line and connected to a new potentiometer and a new Weston cell, both from Leeds and Northrup, and both never put in the hands of students. The milliammeter, like the voltmeter, was calibrated with this apparatus. The calibration of the voltmeter was repeated several times, and although at first there were slight changes, due to elastic after-effects in a new bifilar suspension, the readings at the time these isochromats were taken, allowing for fluctuations and all other disturbing factors, must be better than 1/10 of a per cent.

The other important point is that the x-ray beam was limited by only one slit, placed near the crystal. The slit in front of the ionization chamber was wider than the beam entering it, and the one near the tube was wider than the focal spot, so that neither of them could limit the width of the x-ray beam. These precautions are needed because, as one may predict from space-charge theory, or prove by experiment, the focal spot is wider at low voltages and high currents than at high voltages and low currents.

The cathode rays, allowing for electrostatic deflection, probably strike the target at about 10° to the axis of the tube, and the thin glass window

[1] Bull. N. R. C., *1*, No. 7, Dec., 1920.

through which the x-rays were taken out was at about 100° from the anode end. This makes the angle of the x-rays from the line of the cathode rays 110°.

## III. The Correction for Scattering.

The correction mentioned above, for x-rays scattered by the crystal, is like the correction of an ordinary spectro-photometric measurement for stray light of other colors. Here it was estimated by setting the crystal to reflect some frequency to be used for an isochromat, and then moving the ionization chamber to various positions on each side of the reflected rays, and measuring the rays scattered to these positions. Plotting these scattered rays against the chamber angle, it was usually easy to interpolate graphically for the scattered rays at the reflecting position.

The correction, while often about 10 times as large at twice the quantum voltage as at the quantum voltage itself, was relatively unimportant except near the quantum voltage, where the reflected rays were very weak. Elsewhere it rarely amounted to more than one per cent. of the reflected rays.

There were, however, certain very peculiar effects in this scattering, where lines appear, like weak reflected lines at angles different from the normal reflection. Some of these "ghosts," as we may call them by analogy to those from a grating, could be traced by their excitation potentials and the forms of their isochromats, to small bits of crystal out of the normal alignment, reflecting sometimes rays of the continuous spectrum and sometimes the characteristic lines. Other ghosts, however, followed laws unlike those of such reflections. Duane[1] has described similar effects from a potassium iodide crystal, which he ascribed to fluorescence of the iodine, but these are of some other origin. The ones found here may possibly be due to fragments of crystal that are bent, as well as out of alignment. They are mentioned here chiefly because one of them, unfortunately, moved into coincidence with the reflected beam at small angles. It spoiled the isochromats with quantum voltages above 30 kv. ($\lambda = 0.4117$ Å.), at least for any accurate interpretation. Probably those with quantum voltages 40 and 50 contain errors as large as 3 or 4 per cent., at 70 kv., and are correct only below about 50 and 60 kv., respectively.

An important fact about the continuous scattering, as distinguished from these ghosts, is that some very faint rays are found, at any frequency, below the quantum voltage. Such rays, however, appear to

[1] W. Duane, Amer. Phys. Soc., Meeting of April, 1922.

be due to scattering only. The importance of this is that if any rays were emitted by the mechanism of the old pulse theory, the only way we could detect them would be by their presence under such conditions. We may now say that the intensities of any such rays are well under one per cent. of the rays found at the same frequencies at twice the quantum voltage. A few measurements with tungsten at 0.3 Å., made to test this point, gave an upper limit 1/10,000 of the corresponding intensity.

## IV. The Correction for Target Absorption.

The target absorption, as explained in the preceding paper, is not predictable accurately from any theory now at hand. The measurements recorded there show the absorption at the $K$ limit, but elsewhere we are dependent on rough estimates. Following Ham,[1] and Davey,[2] who found mean depths of excitation, for all frequencies together, increasing in proportion to the voltage, we may as well assume the same here, in a form modified to fit the requirements of a single frequency and the results of the preceding paper. For this, we shall assume a mean depth law for any frequency, with the same algebraic form as at the absorption limit and leading to the same mean depth at a high voltage for rays of any two frequencies. Specifically, the law assumed was

$$\frac{I_{cor} - I_{obs}}{I_{obs}} = \mu\bar{x}, \qquad \text{where} \qquad \bar{x} = gV\left(1 - e^{-15\left(\frac{V}{Hv}-1\right)}\right),$$

$$g = 0.049\,\frac{\text{micron}}{\text{kilovolt}} \qquad \text{and} \qquad H = \frac{h}{e}.$$

This correction law fits the data at the absorption limit within about one per cent., and is probably as good as anything now available for other frequencies. The absorption coefficients, $\mu$, were taken from data by Richtmyer,[3] and were all found by interpolation except the values at the absorption limit itself, which required short extrapolations. These values were assumed to be 752 cm.$^{-1}$ and 113 cm.$^{-1}$, the ratio between them being 6.65.

## V. Reduction to Comparable Scales.

To compare the different isochromats, we have corrected them first for scattering and then for target absorption. Then we have reduced them all to corresponding scales of voltage and intensity. The voltage, $V$, has been expressed in terms of the ratio, $V/Hv$ (where $H = h/e$

[1] W. R. Ham, Phys. Rev., *30*, 1, Jan., 1910.
[2] W. P. Davey, J. Franklin Inst., March, 1911.
[3] F. K. Richtmyer, Phys. Rev., *18*, 13, July, 1921.

$= 4.117 \times 10^{-15}$ volt seconds), the intensity in terms of the ratio $I/I_2$ where $I_2$ is the intensity at $V/Hv = 2$. Thus all the graphs start at the point 1, 0, and go through the point 2, 1.

Beyond this point, it is useless to follow them, because when $V = 2Hv$, rays are excited whose wave-length is half that of the one in question, and the second order reflection of that wave-length is mixed with the rays to be measured. An attempt was made to eliminate this by the use of a (111) face of fluorite, but no fluorite could be found that was regular enough to use without serious complications. Therefore the present results run only to the point 2, 1. Some, in fact, stop short of that, because gas in the tube prevented the use of any voltages above about 70 kv., and the ones starting at 40 and 50 kv. are unreliable above about 50 and 60, respectively, because of the unknown effect of the "ghost" that is mixed with them above those voltages.

The results are presented diagrammatically in Fig. 1. Each iso-

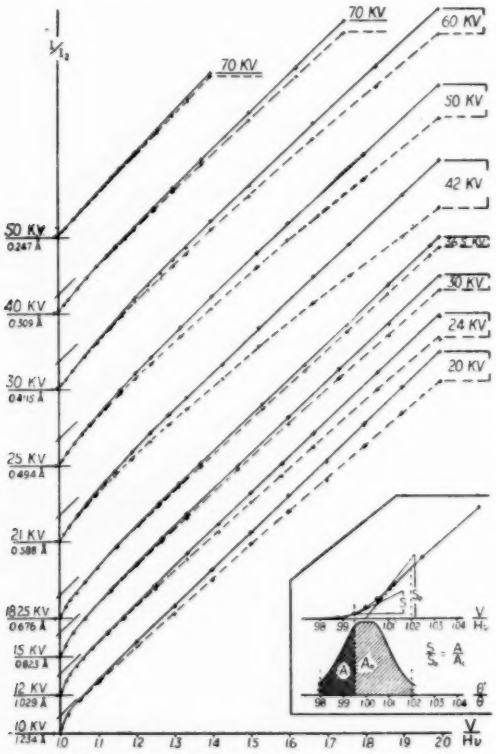


**Fig. 1.**

Molybdenum isochromats at 110° from the line of the cathode rays. Full lines, corrected for absorption, dotted lines, observed.

chromat is labeled in terms of its quantum potential, $H\nu$, and its wave-length. The wave-lengths are chosen to give round numbers for $H\nu$, except where such numbers would bring the wave-lengths too near the characteristic lines. 18.25 kv. gives a wave-length between the $\alpha$ and $\beta$ lines, at the point where the stray rays from these lines are a minimum. This graph may be slightly distorted by such rays, making it a little too straight, but the effect is probably not over 1 or 2 per cent., if that much. The 21 kv. wave-length is on the short-wave side of the absorption limit, as will be seen from the size of its absorption correction, as compared to that of 18.25, while the 15 kv. is for a longer wave-length than $K\alpha$.

All these corrected graphs are straight, except for the downward curvature near the foot. The similarity in this respect is especially noteworthy when compared to the differences in the dotted graphs, that represent the same measurements not corrected for absorption.

## VI. The Intercepts on the $V$ Axis.

At the foot of each isochromat, the graph should strike the axis at exactly the calculated potential, provided that all the rays used were of exactly the intended wave-length. But of course they can not be so, because of the finite widths of the source and slit. Instead, there is a distribution of wave-lengths over a finite angle, and each isochromat rounds off concave upward, for a short range at the foot.

If the rays were uniformly distributed over their range of glancing angles, $d\theta$, then the width of the foot of the isochromat would be $dV$, where

$$\frac{dV}{V} = \frac{d\lambda}{\lambda} \text{ or nearly } \frac{d\theta}{\theta}.$$

Thus on the ratio scale, $V/H\nu$, the width of the foot, being $dV/H\nu$, should be inversely proportional to $\theta$, or directly proportional to $\nu$, as one may see it is, qualitatively at least, in Fig. 1.

Practically, we have no such simple distribution over the range $d\theta$ as this. The actual distribution depends on the distribution of cathode rays in the focal spot and the nature of the imperfections, if there are any, in the crystal. But it can be found experimentally, by plotting a short piece of a spectrum that includes the $K\beta$ line. Assuming the line to be truly monochromatic, its form in the spectrum graph represents accurately (although reversed on the scale of angles) the distribution of energy that would occur over the range $d\theta$ if the crystal were set at some point in the continuous spectrum. If this distribution were uni-

form, then the $\beta$ line would appear on the graph as a tall rectangle. Practically, however, the $\beta$ line has a form more like a probability curve, as one might expect from the factors that enter into it. With the rays limited by a 2.5-mm. focal spot and a single slit of 0.55 mm. at 77 cm. distance, the theoretical extreme width is 13.5′ of arc, and the half-value width should be considerably less. Practically, the extreme width was about that amount, but very indefinite, a small trace of line radiation being found many minutes away from the main part of the line, as described in the preceding paper, where it was explained as a result of crystal imperfections. The half-value width was about 7′, and in every case the width of the foot of the isochromat was about as calculated.

To make sure of this point, a few isochromats were taken with two slits, one as before, and the other 12 cm. from the target and 1.0 mm. wide. With the two slits, the theoretical form of the $\beta$ line is a figure with a flat top and straight, sloping sides. If the slit widths are $s_1$ and $s_2$, at a distance $D$, the width of the flat top is $(s_1 - s_2)/D$, each sloping side $s_2/D$, the half-value width $s_1/D$ and the extreme width $(s_1 + s_2)/D$. These values, with the above data, are 2.4′, 2.9′, 5.3′ and 8.2′ respectively. The experimental values of the first three were 2.0′, 3.5′, and 5.3′, and for the last, if we cut off the faint spreading at the base of the line by crystal imperfections, we should have 8.5′. This remarkably close agreement indicates a very good crystal. However, another crystal, almost as good, to all outward appearances, gave a rounded $\beta$ line curve under the same conditions, that did not fit the theory nearly so well. Perhaps this means the crystal we used was better, and perhaps neither of them was as good as the above results indicate.

With the beam thus limited, we could not make any great changes of potential without causing slight errors from changes of the focal spot width, and consequently of the fraction of the cathode rays that were within the lines of the slits. These isochromats were therefore used only to check the lowest few per cent. of the voltage range. At the foot, assuming the graph for truly homogeneous rays to be nearly straight for a short range, we may predict the form of the experimental graph as follows: Transfer the $\beta$ line graph, unchanged, to the angle $\theta$, where the isochromat is to be taken. It then represents the graph one would get for another line, at that angle, if such a line existed. Then reverse it on the scale of angles, to represent the distribution of rays in a single setting in the continuous spectrum. Next, divide each angle, $\theta'$, in this last graph, by $\theta$, thus expressing the distribution of rays in the beam on

a relative basis, as in the insert in Fig. 1. Now suppose $V/H\nu$ is given some definite value, say 0.996. The fraction of the rays whose quantum voltage is then exceeded is found by drawing an ordinate in this modified $\beta$ line graph at $\theta'/\theta = 0.996$, and comparing the area, $A$, to the left of this ordinate, with the whole area $A_0$. If, now, the slope of the isochromat for a truly monochromatic beam is $S_0$, that of a beam in which a fraction $A/A_0$ of the rays have their quantum voltage exceeded must be $S$, where

$$\frac{S}{S_0} = \frac{A}{A_0}.$$

Experimentally, this is just what occurs, as illustrated in Fig. 1, which is taken from the data at $H\nu = 40$ kv.

The value of $h$ assumed in this calculation was that given by Birge,[1] in 1919, as an average from all the evidence then at hand. It is

$$h = (6.5543 \pm 0.0025) \times 10^{-27} \text{ erg. sec.},$$

with

$$e = 4.774 \times 10^{-10} \text{ e.s.u.},$$

If

$$c = 2.9986 \times 10^{10} \frac{\text{cm.}}{\text{sec.}},$$

this means

$$H = \frac{h}{e} = 4.117 \times 10^{-18} \text{ kv. sec.}, \quad \text{or} \quad V\lambda_{\min} = \frac{hc}{e} = 12.345 \text{ kv. Å.}$$

The present result depends on the accuracy with which our voltages could be reproduced, allowing for all fluctuations ordinarily produced by all causes. This was at least as good as 1/10 per cent. Another factor was our scale of angles. The zero of this scale was set by taking the middle of the $\beta$ line to be 5° 59′ 10″, choosing this as a weighted mean of the values 5° 59′ 37″ and 5° 58′ 55″ calculated from data by Overn [2] and by Duane and Patterson,[3] respectively. In view of the great accuracy of the data summarized by Birge, this work adds nothing to our knowledge of $h$; but it does justify fully our taking the intercept thus calculated as that of the graph for truly monochromatic rays, of the same frequency as the average in the real beam, and considering this point on the graph at least as accurate as any other.

## VII. An Empirical Equation.

An empirical equation for an isochromat, used previously by one of us,[4] is

$$I(V, \nu)d\nu = k(\nu)\{(V - H\nu) + H\nu p(\nu)(1 - e^{-q(\nu)\left(\frac{V}{H\nu} - 1\right)}\}d\nu$$

[1] R. T. Birge, Phys. Rev., *14*, 361, Oct., 1919.
[2] O. B. Overn, Phys. Rev., *18*, 350, Nov., 1921.
[3] W. Duane and R. A. Patterson, ibid., *19*, 542, May, 1922.
[4] See Bulletin of the N. R. C., *1*, No. 7, Dec., 1920, for a discussion of this equation

In this equation, $k(\nu)$, $p(\nu)$ and $q(\nu)$ are all functions of $\nu$, to be determined, but are of course constant for any one isochromat. The second term in this formula is the one giving the curvature to the isochromat, and it becomes constant in the linear part. To find $p$ and $q$, we extrapolated the linear part of the curve back to the ordinate at $V = H\nu$. If we call the ordinate of any point on this straight line $I'(V, \nu)$, then

$$I'(V, \nu) = k(\nu)\{(V - H\nu) + H\nu p(\nu)\}.$$

Thus the intercept is

$$I_1' = I(H\nu, \nu) = k(\nu)H\nu p(\nu),$$

while

$$I_2 = I(2H\nu, \nu) = k(\nu)\{(H\nu) + H\nu p(\nu)\}.$$

Solving for $p$, we have

$$p(\nu) = \frac{I_1'}{I_2 - I_1'}.$$

These intercepts, as found experimentally, are shown in Fig. 1, the 40- and 50-kv. isochromats being omitted because of the unreliability in these data, mentioned above, which affects calculations of this type especially badly.

To find $q(\nu)$, we have

$$I'(V, \nu) - I(V, \nu) = I_1' e^{-q(\nu)\left(\frac{V}{H\nu} - 1\right)}.$$

Thus to find $q$, we simply looked for the points where this difference equalled $I_1'e^{-1/2}$, $I_1'e^{-1}$ and $I_1'e^{-2}$. The values of $V/H\nu$ at these points should be

$$\left(1 + \frac{1}{2q}\right), \quad \left(1 + \frac{1}{q}\right) \quad \text{and} \quad \left(1 + \frac{2}{q}\right).$$

In general, the values of $1/q$ thus found are not far apart, showing that the formula fits the curves fairly well, and in fact if the mean of the three is chosen for $q$, the calculated values of $I$, for the higher frequencies, always agree with the experimental graphs to within an amount equal to $\frac{1}{2}$ per cent. of $I_2$. At the lower frequencies there is a slight systematic deviation, in the direction of too quick a decrease of $(I' - I)$ at first, and too slow later, but the difference is never over about 1 per cent. of $I_2$. This systematic deviation is nearly if not quite within the limits of experimental error; but it appeared also in the previous work on rhodium and platinum, and in Wagner's work[1] on copper and platinum at potentials below 10 kv., and in some preliminary work here on copper and tungsten. So it may very well be real; yet it is doubtful,

[1] E. Wagner Ann. der Phys., 57, 104, Dec., 1918.

because none of these data, except the present ones on molybdenum, have yet been corrected for target absorption.

To fit the isochromats with a formula containing $p$ and $q$ expressed algebraically, the experimental values of these functions were plotted against $H\nu$, in Fig. 2. The $p(\nu)$ data were fitted fairly well by a formula

$$p(\nu) = \sqrt{\frac{\nu}{\nu_1}},$$

where $\nu_1$ = constant = $9.7 \times 10^{22}$ sec.$^{-1}$ and $H\nu_1$ = 4,000 kv.

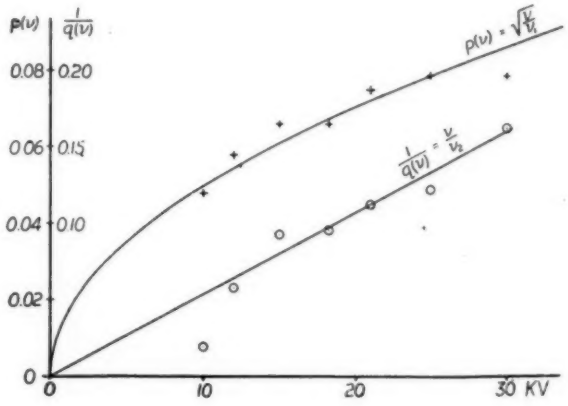


Fig. 2.

Data on $p(\nu)$ and $1/q(\nu)$, plotted against $H\nu$, with graphs of assumed laws.

Likewise the data for $q(\nu)$ were fitted fairly well by a formula

$$q(\nu) = \frac{\nu_2}{\nu},$$

where $\nu_2$ = constant = $4.5 \times 10^{19}$ sec.$^{-1}$ and $H\nu_2$ = 187 kv. With these values for $p$ and $q$, the formula does not fit the data quite as well as with the empirical values, but still is rarely off by more than 1 or 2 per cent. of $I_2$.

## VIII. Reduction to Isochromats for an Infinitely Thin Target.

In a thick target, such as the molybdenum block used here, the x-rays are not all emitted by cathode rays of the same speed, even though the potential applied to the tube is constant. Not one cathode ray in a thousand, under most conditions, emits any x-rays hard enough to get out of the tube. Instead of losing energy by large quanta in that way, most of them seem to lose it gradually by ionizing the atoms. Thus the target must contain electrons of all speeds, each one capable of producing

x-rays appropriate to its speed. Only in an extremely thin target would we find anything like uniformity of speeds. From the viewpoint of radiation theory, such a target would be the most interesting.

It is also, however, the most difficult to use. Fortunately, by a method outlined in a previous paper,[1] we can calculate what such a target would give, in terms of the $V$ derivative of $I$. In that paper, the result was expressed for a target of such thickness that any cathode ray would strike just one atom. There is, however, some question as to what constitutes "striking" an object of such indefinite boundaries as an atom, so it may be better to express the result in terms of the *intensity per electron and per unit thickness* from a target of infinitesimal thickness. The symbol $i(V, \nu)$ will be used here for this latter quantity, as $I(V, \nu)$ is used for the intensity per electron from the thick target. Its dimensions are therefore those of $I \div$ length, and it is to that extent different from the $i$ of the previous paper.

By the same sort of reasoning used there, it appears that

$$i(V, \nu) = D_V I(V, \nu) \left( - \frac{dV_s}{ds} \right)_{s=0},$$

where $V_s$ is the potential corresponding to a cathode ray's energy after penetrating a distance $s$, this $s$ being measured not along the line of $x$, but along the crooked path of the individual cathode ray.

Although the Thomson-Whiddington law fails to give the depth of penetration, $x$, except for the few electrons that go straight, it is fairly probable that the path distance, $s$, can be found by this law. Assuming this, and stating the law in the form

$$V_s^2 = V^2 - bs,$$

we have

$$\frac{dV_s}{ds} = - \frac{b}{2V_s}.$$

Then differentiating the expression for $I(V, \nu)$ given in the last section, we find

$$D_V I(V, \nu) = k(\nu)\{1 + p(\nu)q(\nu)e^{-q(\nu)\left(\frac{V}{H\nu} - 1\right)}\}$$

or, with the present values of $p$ and $q$,

$$i(V, \nu) = \frac{bk}{2V}\left\{1 + \frac{\nu_2}{\sqrt{\nu_1 \nu}} e^{-\frac{\nu_2}{\nu}\left(\frac{V}{H\nu} - 1\right)}\right\}.$$

In this expression, the only unknown quantity is $k(\nu)$. To find it,

[1] D. L. Webster, PHYS. REV., 9, 220, March, 1917.

we may use a method previously described,[1] dependent on the fact that the total x-ray energy is given by the equation $E(V) = \int_0^{V/H} I(V, \nu)d\nu$.

If $E(V)$ is accurately proportional to $V^2$, as is usually assumed, and if $p(\nu)$ and $q(\nu)$ were constants, this equation could be satisfied only by making $k(\nu)$ a constant. The value of $k$ would then be given by the equation

$$E(V) = k\frac{V^2}{H}\left\{\frac{1}{2} + \frac{p}{2} - p\int_0^1 xe^{-q\left(\frac{1}{x}-1\right)}\,dx\right\}$$

or approximately

$$E(V) = \tfrac{1}{2}k\frac{V^2}{H}\left\{1 + p - 2\frac{p}{q}\right\}.$$

With $p$ and $q$ variable, as we have them in this case, these formulas could apply only if the values used for $p$ and $1/q$ are certain weighted

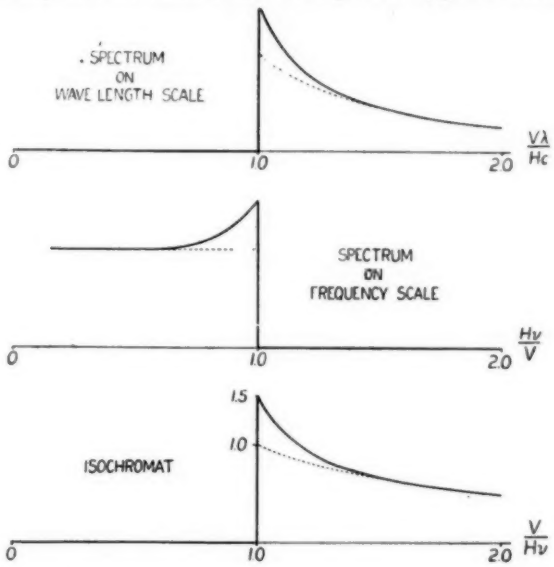


Fig. 3.
Typical thin target spectrum and isochromats, with values of $p$ and $q$ taken from isochromat at $\lambda = 0.412$ Å.

means of the values at all frequencies involved. Such values, however, would be small, that for $p$, up to 30 kv., for example, being probably about 0.06, with $1/q$ about 0.10. This would make

$$E(V) = \tfrac{1}{2}k\frac{V^2}{H}\{1 + 0.06 - 2 \times 0.06 \times 0.10\}$$

$$= \tfrac{1}{2}k\frac{V^2}{H}\{1 + 0.05\}.$$

[1] D. L. Webster, Proc. Nat. Acad., 5, 163, May, 1919.

The whole influence of the $p$, $q$ term in $I$ is therefore to change $k$ by only about 5 per cent. Thus even if $p$ and $q$ vary considerably, the effect on $k$ is small and may easily be as small as the errors in the $V^2$ law for $E$. So it hardly seems practical to attempt a more accurate estimate of $k$ from the present data.

Accepting $k$ as a constant, the thin target function may be expressed by the equation given above, or in terms of $\lambda$,

$$j(V, \lambda)d\lambda = \frac{bkc}{2V\lambda^2}\left\{1 + \frac{\sqrt{\lambda_1\lambda}}{\lambda_2}e^{-\frac{\lambda}{\lambda_2}\left(\frac{V\lambda}{Hc}-1\right)}\right\}d\lambda,$$

where $\lambda_1 = 0.0031$ Å. and $\lambda_2 = 0.066$ Å. This gives spectra and isochromats of the general type shown in Fig. 3.

## IX. Electron Collisions and Radiation.

Assuming that each collision of a cathode ray with an atomic electron must either cause radiation of a whole quantum or none at all, we can find the probability of radiating any particular frequency. For if an electron penetrates a distance $ds$, radiating energy $i(V, \nu)d\nu ds$ in the range $d\nu$, the number of radiating collisions is

$$\frac{i(V, \nu)d\nu ds}{h\nu}.$$

Presumably, the closer the cathode electron approaches to an atomic electron, the greater will be the chance of exciting the radiating mechanism, whatever it may be. Let us assume tentatively that the distance of approach is the only factor involved; and let us specify it in terms of the distance $r$ from the atomic electron to the straight line that the cathode ray was moving on before the collision. Thus we avoid any assumptions as to what forces deviate it from that line. In a target of thickness $ds$, with $n$ electrons per unit volume, the number of electrons lying at distances between $r$ and $r + dr$ from the straight line will be, on the average,

$$2\pi nrdrds.$$

In terms of probabilities, we may say that the probability of any electron radiating a frequency $\nu$ to $\nu + d\nu$ in a distance $ds$ is

$$\frac{i(V, \nu)d\nu ds}{h\nu} = \frac{bk}{2h}\frac{\left\{1 + \frac{\nu_2}{\sqrt{\nu_1\nu}}e^{-\frac{\nu_2}{\nu}\left(\frac{V}{H\nu}-1\right)}\right\}d\nu ds}{V\nu}.$$

Defining $r$ now as the atomic distance giving this frequency and noting that

$$\nu = \frac{V}{Hr}$$

only on a direct hit, with $r = 0$, we have

$$\int_0^r 2\pi n r dr = \int_\nu^{V/H} \frac{i(V, \nu)d\nu}{h\nu}.$$

Neglecting the variability of $k$, $p$ and $q$, and approximating in the integration much as we did for $E(V)$, this becomes

$$\pi n r^2 = \frac{bk}{2h} \frac{\log \frac{V}{H\nu} + p(1 - e^{-q(\frac{V}{H\nu}-1)})}{V}.$$

In conclusion it must be noted that the above expression for the probability of radiating a frequency $\nu$ in the distance $ds$ depends on the $V^2$ law for $E(V)$ and the Thomson-Whiddington law as applied to the crooked path of an individual cathode ray. The expression connecting $r$ with $V$ and $\nu$ therefore involves these assumptions as well as the assumption that $\nu$ is determined by $V$ and $r$ alone. If the $V^2$ law and the Thomson-Whiddington law prove incorrect, the above experimental results and methods of calculation can be used with whatever modified forms of these laws are accepted. Meanwhile any theory that uses these laws in attempting to explain this spectrum should start with a probability law approximately equivalent to that given here.

We wish to express here our gratitude to Dr. W. D. Coolidge for the special Coolidge tube used in the work of this paper and the preceding one, and to Messrs B. G. Stuart and S. W. Borrow for the tedious but necessary work of regulating the D.C. generating plant while the readings were taken, as well as for making a large part of the apparatus, and to the Rumford Committee of the American Academy of Arts and Sciences for very generous financial assistance.

STANFORD UNIVERSITY,
CALIFORNIA,
August 29, 1922.

# CHARACTERISTIC *L* ABSORPTION OF X-RAYS FOR ELEMENTS OF ATOMIC NUMBERS 62 TO 77.

By J. M. Cork.

Abstract.

**Characteristic L x-ray aborption wave-lengths for nine elements of atomic numbers 62 to 77.**—Since the *L* absorption wave-lengths had been determined for elements of atomic numbers 55 to 60, 74, and 78 to 92, it was of interest to fill in the gaps. Accordingly compounds of *samarium* (62), *gadolinium* (64), *dysprosium* (66), *erbium* (68), *ytterbium* (70), *tantalum* (73), *tungsten* (74), *osmium* (76) and *iridium* (77) were precipitated upon filter paper and placed in the path of x-rays from the tungsten target of a Coolidge tube. In each case the three *L* absorption bands together with the emission lines of *W* were photographed, using a calcite crystal which was rotated with a constant angular velocity. The wave-lengths and the frequency numbers divided by the Rydberg constant, $\nu/N$, are tabluated. *The energy levels within the atoms* corresponding to the different absorption limits computed in terms of $\nu/N$ from the absorption and emission frequencies, are also given. The regular doublet differences $\Delta(\nu/N) = (\nu_{L_2} - \nu_{L_1})/N = L_2 - L_1$ are found to agree well with the values calculated from the Sommerfeld formula.

**The variation of the regular doublet frequency differences $L_2 - L_1$, $M_2 - M_1$, $M_4 - M_3$ with atomic number** is given very closely by the series expressions developed by Sommerfeld. For elements of high atomic numbei, $Z$, these series do not converge very rapidly. For the range of elements mentioned in this paper the empirical expression $\Delta(\nu/N) = KZ^5$ is found to hold within the experimental limits where $K$ has the following values: $4.44 \times 10^{-8}$ for $L_2 - L_1$, $1.97 \times 10^{-9}$ for $M_2 - M_1$, and $9.60 \times 10^{-9}$ for $M_4 - M_3$.

**Suggested notation for x-ray emission lines.**—Instead of the present conflicting notations, it is suggested that the symbol for each emission line designate the initial and final energy levels; for example the line produced by an electron shifting to the $L_1$ from the $M_5$ orbit might be denoted by $L_1\beta_5$ instead of $Ll$ or $L_\epsilon$.

THE three *L* absorption wave-lengths for elements of atomic numbers 55 to 60 have been determined by Hertz;[1] and for elements of atomic numbers 74 and 78 to 92 by deBroglie[2] and Duane.[3] As these data are of great significance in building theories of the inner atomic structure, alternate elements in the gap, atomic numbers 62 to 77 have been investigated.

Most of the elements investigated are rare earths, compounds of which were isolated by Professor James of New Hampshire State College. The compound of the element used, shown in Table I., was uniformly

[1] Hertz, Z. fui Phys., 3, 1, p. 19.
[2] deBroglie, J. de Phys., 6, p. 161.
[3] Duane, Proc. Nat. Acad. Sci., 6, p. 509.

distributed upon a filter paper and placed in the path of the x-ray beam at the first slit between the x-ray tube and the calcite crystal. The crystal was rotated by means of a clock mechanism over a small arc, and the reflected x-ray beam was examined photographically.

TABLE I.

*Compounds Used.*

| At. No. | Element. | Compound. |
|---|---|---|
| 62 | Samarium | Oxalate |
| 64 | Gadolinium | Oxalate |
| 66 | Dysprosium | Oxalate |
| 68 | Erbium | Oxalate |
| 70 | Ytterbium | Oxalate |
| 73 | Tantalum | Tantalic acid |
| 74 | Tungsten | Tungstic acid |
| 76 | Osmium | Osmic acid |
| 77 | Iridium | Chloride |

A Coolidge tube provided with a tungsten target was used as a source of x-rays and there thus appeared upon the photographic plate the emission lines of tungsten as well as the absorption lines of the element under investigation. A 500-cycle generator with step-up transformer was used as the power supply. The secondary of the transformer was connected to the x-ray tube through a kenotron rectifier, while a high voltage condenser was connected in parallel with the x-ray tube. The capacity of the condenser was sufficiently high to result in an almost constant direct voltage being applied to the tube. In most of the work a tube current of 7 milliamperes at 30,000 volts was used. This was found to be about the maximum allowable power input for continuous operation of the tubes. An air blast was directed against the tube to aid in cooling. At this power input a time of exposure of from 30 to 40 hours was necessary to secure satisfactory plates. This long time was required because x-rays of the wave-lengths worked with were largely absorbed in the glass walls of the x-ray tube; the time of exposure necessary would have been greatly reduced by using a tube provided with a thin window.

The wave-lengths of the tungsten emission lines have been determined by Overn,[1] Duane,[2] Siegbahn,[3] and others, with very good agreement for the more prominent lines. These were used as reference lines in measuring the wave-lengths of the absorption edges. The values of the wave-lengths used, expressed in Ångstrom units, are shown in Table II.

[1] Overn, PHYS. REV., 9, 137, 1919.
[2] Duane, PHYS. REV., 15, 532.
[3] Siegbahn, Ph. Z., 20, p. 533.

TABLE II.

*X-ray Spectrum of Tungsten.*

| Wave-lengths Observed by | | | Wave-lengths Used. | Notation of | | Notation Suggested. |
|---|---|---|---|---|---|---|
| Overn. | Siegbahn. | Duane. | | Siegbahn. | Sommerfeld. | |
| 0.9168 | | | 0.9168 | | | |
| 1.0263 | 1.02647 | 1.0261 | 1.0263 | $\gamma_4$ | $\psi$ | $L_3\delta_3$ |
| 1.0596 | 1.05965 | 1.0596 | 1.0596 | $\gamma_3$ | $x$ | $L_3\gamma_8$ |
| 1.0659 | 1.06584 | 1.0655 | 1.0657 | $\gamma_2$ | $x'$ | $L_3\gamma_6$ |
| 1.0967 | 1.09533 | 1.0965 | 1.0960 | $\gamma_1$ | $\delta$ | $L_2\gamma_4$ |
| 1.1302 | 1.1284 | | 1.1290 | $\gamma_5$ | $\kappa$ | $L_2\gamma_7$ |
| 1.2434 | 1.24191 | 1.24193 | 1.2420 | $\beta_2$ | $\gamma$ | $L_1\gamma_3$ |
| 1.2598 | 1.2600 | 1.2601 | 1.2600 | $\beta_3$ | $\varphi$ | $L_3\beta_3$ |
| 1.2793 | 1.27917 | 1.2789 | 1.2792 | $\beta_1$ | $\beta$ | $L_2\beta_2$ |
| 1.2872 | 1.2871 | | 1.2872 | $\beta_6$ | $i$ | $L_1\gamma_7$ |
| 1.2984 | 1.29874 | 1.2985 | 1.2986 | $\beta_4$ | $\varphi'$ | $L_3\beta_4$ |
| 1.4731 | 1.47348 | 1.4731 | 1.4732 | $\alpha_1$ | $\alpha$ | $L_1\beta_1$ |
| 1.4839 | 1.4845 | 1.4839 | 1.4840 | $\alpha_2$ | $\alpha'$ | $L_1\beta_2$ |
| | 1.67505 | 1.6756 | 1.6753 | $l$ | $\epsilon$ | $L_1\beta_5$ |

A distance of 0.1 cm on the plates corresponded to a difference in wave-length of about .01 Ångstrom unit. The probable error in the measurement of the lines was about .002 cm, corresponding to an accuracy of about .0002 A. However the wave-lengths of some of the tungsten emission lines are not agreed upon to that degree of accuracy. In a few cases the absorption-limit falls very close to an emission line. For the longer wave-lengths where extrapolation is necessary, the error in $L_1$ and $L_2$ may be as large as .002 A, and for $L_3$, which is not so clear, the error may be larger.

TABLE III.

| Atomic Number. | $A_1$. | | | $A_2$. | | | $A_3$. | | |
|---|---|---|---|---|---|---|---|---|---|
| | $\lambda$. | $\nu/N$. | $(\nu/N)^{1/2}$. | $\lambda$. | $\nu/N$. | $(\nu/N)^{1/2}$. | $\lambda$. | $\nu/N$. | $(\nu/N)^{1/2}$. |
| 62..... | | | | 1.701 | 535.7 | 23.14 | 1.608 | 566.7 | 23.80 |
| 64..... | 1.699 | 536.4 | 23.16 | 1.550 | 587.9 | 24.25 | 1.470 | 619.9 | 24.89 |
| 66..... | 1.576 | 578.2 | 24.05 | 1.435 | 635.0 | 25.20 | 1.362 | 669.1 | 25.87 |
| 68..... | 1.478 | 616.5 | 24.83 | 1.336 | 682.1 | 26.12 | 1.265 | 720.4 | 26.84 |
| 70..... | 1.386 | 657.5 | 25.64 | 1.242 | 733.7 | 27.09 | 1.171 | 778.2 | 27.90 |
| 73..... | 1.253 | 727.3 | 26.98 | $1.111_8$ | 819.6 | 28.63 | 1.058 | 861.3 | 29.35 |
| 74..... | $1.211_2$ | 752.3 | 27.43 | $1.071_8$ | 850.2 | 29.17 | 1.023 | 890.8 | 29.85 |
| 76..... | 1.138 | 800.7 | 28.30 | $.998_5$ | 912.6 | 30.21 | $.951_5$ | 957.7 | 30.94 |
| 77..... | $1.103_6$ | 825.7 | 28.74 | .965 | 944.3 | 30.73 | $.919_8$ | 991.0 | 31.47 |

Table III. shows the mean values of wave-lengths observed, expressed in Ångstrom units. In addition, the values of $\nu/N$ and of the square root of $\nu/N$ are given, where $\nu$ is the number of waves per cm and $N$ is

the Rydberg constant

$$\frac{2\pi^2 e^4 m}{h^3 c} = 109{,}740,$$

$e$ and $m$ being respectively the charge and mass of an electron, $h$ the Planck constant $6.55 \times 10^{-27}$ erg sec, and $c$ the velocity of light.

TABLE IV.

| At. No. | $L_2 - L_1$. | Calc. $\Delta(\nu/N)$. | $L_\beta - L_{\alpha'}$. |
|---|---|---|---|
| 62 | | 43.85 | 43.95 |
| 64 | 51.5 | 50.65 | 50.64 |
| 66 | 56.8 | 58.25 | 58.27 |
| 68 | 65.6 | 66.66 | 66.80 |
| 70 | 76.2 | 76.29 | 76.24 |
| 73 | 92.3 | 92.34 | 92.66 |
| 74 | 97.9 | 98.46 | 98.54 |
| 76 | 111.9 | 111.33 | 111.08 |
| 77 | 118.6 | 118.30 | 118.64 |

Table IV. shows the $L_2 - L_1$ (regular doublet) frequency difference expressed as $\Delta\nu/N$ compared with values computed from the Sommerfeld formula,[1] and the frequency difference of the $L_\beta$ and the $L_{\alpha'}$ emission lines. The agreement of the three columns is within experimental limits.

The Sommerfeld formula was developed on the assumption that the stationary states of the electrons within the atom are characterized by two quantum numbers. One is called the azimuthal quantum number $n$ which has positive integral values, zero excluded; the other is called the radial quantum number $n'$ and may be zero or a positive integral number. For electrons in the $L$ shell the sum of $n$ and $n'$ is taken as 2. This leads to two possible modes of rotation for the electrons, in one of which, $n = 2$, $n' = 0$, the electronic path is circular, while in the other, $n = 1$, $n' = 1$, the path is an ellipse.

The second postulate states that the frequency of the radiation emitted or absorbed by atoms is determined by the total energy difference between the initial and final states of the atom doing the emitting or absorbing:

$$W_f - W_i = h\nu. \tag{1}$$

Sommerfeld showed that although the quantum sum for electrons characterized by $n = 2$, $n' = 0$ and $n = 1$, $n' = 1$ is the same, if the variation of mass with velocity as required by relativity theory be considered the energy of the two states is not the same, being less in the latter case. The general expression for the total energy of an electron of an orbit characterized by azimuthal quanta $n$ and radial quanta $n'$

[1] Sommerfeld, Atombau, 3d Ed., p. 607.

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is given as:

$$(2)\quad W_{n,\,n'} = hN(E/e)^2\left[\frac{1}{(n+n')^2} + \frac{\alpha^2}{(n+n')^4}\left(\frac{E}{e}\right)^2\left(\frac{1}{4}+\frac{n'}{n}\right) + \cdots\right],$$

where $\alpha^2 = 4\pi^2e^4/h^2c^2 = 5.32 \times 10^{-5}$ and $(E/e)$ is the ratio of the charge on the nucleus to that of an electron. If values of $n = 2$, $n' = 0$ and $n = 1$, $n' = 1$ be substituted in Eq. (2) and the difference of the two equations be divided by $Nh$, the following equation is obtained:

$$(3)\quad \Delta\frac{W}{Nh} = \Delta\frac{\nu}{N} = \left(\frac{E}{e}\right)^4\frac{\alpha^2}{2^4}\left[1 + \frac{5}{2}\frac{\alpha^2}{2^2}\left(\frac{E}{e}\right)^2 + \frac{53}{8}\cdot\frac{\alpha^4}{2^4}\left(\frac{E}{e}\right)^4 + \cdots\right].$$

This equation should then give the difference in $\nu/N$ to be expected in the transfer of electrons from the same initial orbit to these two end orbits or conversely from these two orbits to the same final energy level. By writing in the right-hand member of Eq. (3) $(Z - s)$ for $E/e$, where $Z$ is the atomic number of an element and $s$ an arbitrary parameter, and equating this to $\Delta\nu/N$ obtained by taking the difference of the numbers $\nu/N$ for the $L_\beta$ and $L_{\alpha'}$ emission lines of that element, Sommerfeld obtained an average value for $s$ of 3.5. This value was constant for elements from atomic number 41 to atomic number 92, and was interpreted as a neutralizing effect upon the nucleus due to other electrons of the atom.

When an electron is removed from its orbit to the periphery of the atom the total energy of the system is increased by a definite amount and hence a definite frequency will be absorbed. Thus the $L_1$ absorption frequency means the removal of an electron from the circular orbit $(n = 2, n' = 0)$, while the $L_2$ absorption frequency represents the removal of an electron from the elliptical orbit $(n = 1, n' = 1)$. It should not be expected however that Eq. (2) divided by $hN$ would give the observed values of $\nu/N$ for the absorption limits $L_2$ and $L_1$. For elements of large atomic number the problem is much more difficult. The work in taking an electron to the surface is influenced by the presence of the many other electrons; and the energy of every electron is probably altered by the removal of one of their number. It is the total change in energy that must be considered and to calculate this would require a knowledge of the distribution of all the electrons in the atom. The fact that the difference expression Eq. (3) can be made to fit observed values so well over a wide range of elements indicates that any effect due to other electrons is about the same whether an electron leaves the $L_1$ or $L_2$ levels and hence disappears on taking the difference.

The meaning of the $L_3$ absorption limit is problematical.[1] Its fre-

[1] Wentzel, Z. fur Phys., 6, 2, p. 84 et seq.
Smekal, Z. fur Phys., 5, 2, p. 121 et seq.
Bohr, Z. fur Phys., 9, 1, p. 1.

quency being greater than that of $L_1$ and $L_2$ indicates that the energy change accompanying it is greater than in the two previous cases. Smekal and Wentzel have suggested that the stationary states should be determined by three quantum numbers instead of two, thus making possible a larger number of energy levels for a given quantum sum. Bohr has suggested that the $L$ electrons may be divided into two subgroups; electrons in leaving one of the subgroups give rise to the single $L_1$ absorption frequency, while in leaving the other, which represents a more stable or tightly bound group, it is possible for the electrons left to arrange themselves in two distinct configurations representing different energy totals in the final state. This may perhaps be brought about by electrons travelling in the eccentric orbits of the outer electron shells coming within the $L$ shell.

Figure 1 shows the values of the square root of $\nu/N$, together with

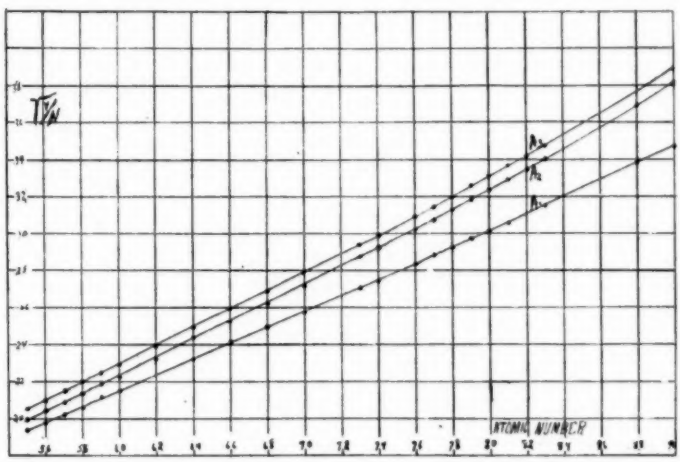


FIG. 1. $\sqrt{\nu/N}$ for $L_1$, $L_2$, and $L_3$ as a function of atomic number.

the values of other observers, plotted as a function of atomic number. By taking into account the nuclear defect due to other electrons and the relativity correction, the deviation of these curves from the straight line Moseley relation may be qualitatively explained. If in Eq. (2) the effect of other electrons be neglected as well as the relativity correction, the first term gives the Moseley relation:

$$\sqrt{\frac{W}{hN}} = \sqrt{\frac{\nu}{N}} = 1/2\left(\frac{E}{e}\right). \tag{4}$$

If values of $(\nu/N)^{1/2}$ were plotted against $E/e$, a straight line of slope 1/2 would be obtained. It is apparent that all three observed curves lie

below this straight line as would be expected if $(Z - s)$ had been used instead of $E/e$. By using additional terms of Eq. (2) the curves would deviate from straight lines with an upward curvature for increasing atomic numbers.

The fact that $\Delta(\nu/N)^{1/2}$ for $L_3 - L_2$ is practically constant would by Bohr's theory indicate that the difference in the neutralizing effect upon the nucleus for the two configurations after the removal of an electron from the $L_2$ subgroup is a constant for a wide range of elements.

By combining the absorption frequencies with the emission frequencies of each element,[1] the energy levels of the various electronic orbits may be determined. Table V. shows these energy levels expressed in terms of

TABLE V. *Values of* $\nu/N$.

| $Z$. | $K$. | $L_1$. | $L_2$. | $L_3$. | $M_1$. | $M_2$. | $M_3$. | $M_4$. | $M_5$. |
|---|---|---|---|---|---|---|---|---|---|
| 62 | 3457 | | 535.7 | 566.7 | | 78.5 | 101.3 | | |
| 64 | 3710 | 536.4 | 587.9 | 619.9 | 90.0 | 92.8 | 116.1 | 126.9 | |
| 66 | 3972 | 578.2 | 635.0 | 669.1 | 99.7 | 101.7 | 126.5 | 138.6 | |
| 68 | | 616.5 | 682.1 | 720.4 | 104.6 | 107.2 | 135.0 | 149.4 | 152.9 |
| 70 | | 657.5 | 733.7 | 778.2 | 111.0 | 114.6 | 149.1 | 165.7 | 172.5 |
| 73 | | 727.3 | 819.6 | 861.3 | 126.9 | 131.1 | 161.9 | 181.7 | 183.7 |
| 74 | 5118 | 752.3 | 850.2 | 890.8 | 133.9 | 138.1 | 167.6 | 189.1 | 207.8 |
| 76 | 5414 | 800.7 | 912.6 | 957.7 | 144.2 | 149.2 | 183.6 | 209.4 | |
| 77 | | 825.7 | 944.3 | 991.0 | 149.9 | 155.3 | 190.2 | 216.4 | |

| $Z$. | $N_1$. | $N_2$. | $N_3$. | $N_4$. | $N_5$. | $N_6$. | $N_7$. |
|---|---|---|---|---|---|---|---|
| 62 | | | | 6.8 | 16.6 | | |
| 64 | | | 13.1 | 14.1 | 31.6 | | |
| 66 | 3.8 | 3.9 | 15.5 | 13.8 | 25.1 | | |
| 68 | .7 | .9 | 13.4 | 13.7 | 26.5 | | |
| 70 | (−1.2) | (−.8) | 12.1 | 13.3 | 32.0 | | |
| 73 | 1.0 | 1.1 | 15.6 | 15.9 | 30.0 | | |
| 74 | 3.2 | 3.0 | 18.5 | 18.4 | 30.9 | 35.8 | 43.4 |
| 76 | 3.6 | 3.4 | 20.1 | 21.3 | | | 44.4 |
| 77 | 4.0 | 4.2 | 21.3 | 22.4 | 38.4 | | 47.9 |

$\nu/N$ for the elements investigated. As some of these computations require the combination of three measurements the errors are correspondingly large. For example $N_1 = L_1 - L_\alpha - M_\alpha$.

From Eq. (3) the variation of the regular doublet difference $L_2 - L_1 = (\nu_{L_2} - \nu_{L_1})/N$ with effective atomic number may be obtained. Similar expressions are developed by Sommerfeld for the regular doublet differences $M_2 - M_1$, $M_4 - M_3$, etc. By effective atomic number is meant the atomic number minus a nuclear defect. This nuclear defect is a constant for any particular doublet over a range of elements from atomic number 41 to atomic number 92; thus 3.5 for $L_2 - L_1$, 13.0 for $M_2 - M_1$,

[1] Hjalmar, Z. fur Phys., 3, 4, p. 262; 7, p. 341.

8.3 for $M_4 - M_3$, etc. As an approximate expression Sommerfeld mentions the first term of the series which on evaluating the constants for $L_2 - L_1$ is $\Delta(\nu/N) = 3.32 \times 10^{-6}(Z - 3.5)^4$. For elements of large atomic numbers the series does not converge rapidly and the first term alone gives values of $L_2 - L_1$ that are about one fourth too small. It may be of interest that the empirical expression $\Delta(\nu/N) = KZ^5$ approximates quite closely the observed values over the range of elements mentioned in this paper for $L_2 - L_1$ and over a wider range for $M_2 - M_1$ and $M_4 - M_3$. $K$ has the following values: $4.44 \times 10^{-8}$ for $L_2 - L_1$, $1.97 \times 10^{-9}$ for $M_2 - M_1$ and $9.60 \times 10^{-9}$ for $M_4 - M_3$.

It is suggested that as soon as an emission line can be definitely related to the transfer of an electron from one orbit to another, this knowledge might well serve as a basis for a notation to replace the present conflicting systems. Such a notation is suggested in Table II. for the tungsten emission lines. The capital letter with subscript gives the end orbit while the Greek letter tells from what group of outer orbits the electron came. The subscript gives the particular orbit of the group. The $L$ group is distinguished by the letter $\alpha$, the $M$ group by $\beta$, the $N$ group by $\gamma$, etc. Thus the line designated by Siegbahn as $Ll$ and by Sommerfeld as $L_\epsilon$ is produced by an electron arriving at the $L_1$ orbit from the $M_5$ orbit. It is accordingly denoted as $L_1\beta_5$. While this notation is more cumbersome, it possesses the advantage of giving complete details without further effort.

UNIVERSITY OF MICHIGAN,
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# THE CRYSTAL STRUCTURES OF THE SYSTEM PALLADIUM–HYDROGEN.

By L. W. McKeehan.

Abstract.

**Crystal structures of the system palladium-hydrogen.**—Palladium in the form of a fine wire, 1/4 mm diam., or of a narrow strip 1/20 mm thick, was more or less saturated with hydrogen and used to diffract x-rays of known wave-length as in the well-known powder method. Two crystal structures were present, both having a face-centered cubic arrangement of atoms. One, that of pure palladium, has a parameter $3.900 \times 10^{-8}$ cm, while the other, that of hydrogen-saturated palladium, has a parameter varying between 4.000 and $4.039 \times 10^{-8}$ cm, depending on the degree of saturation. A value near the upper limit, say $4.036 \times 10^{-8}$ cm, probably corresponds to a *compound* $Pd_2H$, with a *density* of 10.76 gm/cm³. The arrangement of atoms may be as in $Cu_2O$, but there is no x-ray evidence for the positions of the hydrogen atoms. *Stability.* All the evidence so far obtained indicates that in the absence of sufficient free atomic hydrogen, the saturated state is unstable or metastable and that return to the hydrogen-free condition once initiated in any crystal proceeds rapidly to the end; also pure palladium is unstable in the presence of atomic hydrogen.

**Occlusion of hydrogen by palladium.**—A *necessary condition* is the presence of atomic hydrogen which may be supplied by electrolysis or by surface dissociation of hydrogen at high temperatures. The *penetration* into the wire was shown to be relatively slow; in the case of the strip it was somewhat irregular, probably depending on the orientation of the crystals. The crystal evidence provides an *explanation of the variations of electric resistance.* A *bibliography* of 66 titles, mostly 1900–1921, is appended.

THE effect of occluded hydrogen in increasing the electrical resistance of palladium has long been known to be, over a considerable range, a linear function of the amount of hydrogen taken up,[1] and in a study of the factors affecting electrical resistance it seemed of interest to find out, if possible, in what way the hydrogen entered and was held during the process. A direct and available method of attack was that of measuring the changes in crystal structure produced by the process of occlusion. The crystal structure of palladium was first determined by Hull[2] to be based on a face-centered cubic space-lattice. Metal of exceptional purity, samples of which had been analyzed by the same method in this laboratory,[3] was available for the present research.

[1] W. E. McElfresh, Am. Acad., Proc., *30*, 323–335 (1904).
[2] A. W. Hull, Phys. Rev. (2), *17*, 571–588 (1917).
[3] L. W. McKeehan, Phys. Rev. (2), *19*, 537–538; *20*, 424–432 (1922).

There appeared to be some confusion in the considerable literature of palladium-hydrogen systems,[1] as to the possible methods for obtaining high concentrations of hydrogen within the metal. The methods found effective in the present series of experiments furnish support to the theory of the process here advocated, and will therefore be discussed in connection therewith after description of the observed crystal structures.

The powder method of x-ray crystallometry has been described so often that it will suffice to state here that the K-radiation of molybdenum, filtered through zirconium oxide,[2] was used, in which the two photographically important wave-lengths are $0.71212 \times 10^{-8}$ cm and $0.70783 \times 10^{-8}$ cm. The mean radius of the cylinder of photographic film was 20.36 cm. The palladium was either a wire 0.025 cm in diameter or a strip [3] about 0.3 cm wide by 0.005 cm thick. The exposures used were of the order of 500 milliampere-hours. In no case were the grains, even after prolonged annealing, large enough to give separately distinguishable diffraction spots,[4] so that measurements were always made to the edges of smooth bands on the negative. Twenty or more such bands of the principal pattern present were almost always of sufficient intensity to permit their use in calculations, and the mean values of the parameters for the face-centered cubic space-lattices always observed are believed to be correct for each film to within one part in three hundred. Seventeen photographs were taken under various conditions.

There is a fairly well-defined limit in concentration of hydrogen below which the hydrogen is taken up with much greater facility, and the state reached at this limit may therefore with propriety be called the saturated state. If excess hydrogen be taken up the state can be described as supersaturated. With one exception, noted below, supersaturated states were probably not obtained. The method of examination, requiring as it does a relatively long time, is not well adapted to the study of conditions probably as transient as that of supersaturation at ordinary temperatures. Since the change in resistance follows a non-linear law above saturation, it was felt, also, that the lower range of concentration was of chief interest.

In the first experiment a thin strip of metal was, after preliminary annealing, examined first in air and then in a stream of commercial hydrogen, at atmospheric pressure. By what must now be regarded as a happy accident, the strip took up enough hydrogen to saturate it. The parameter of the face-centered cubic lattice of hydrogen-free pal-

[1] See appended bibliography.
[2] W. P. Davey, Optical Soc. America, J., *5*, 479–493 (1921).
[3] L. W. McKeehan, Frank. Inst., J., *193*, 231–242 (1922).
[4] L. W. McKeehan, Frank. Inst., J., *194*, 87–92 (1922).

ladium is [1] 3.900. The pattern here obtained with hydrogen-saturated metal was similar to that of pure palladium, the parameter however being 4.038, or 3.5 per cent greater. This preliminary result has already been reported.[2]

In later experiments with the same strip it was found that after expulsion of the hydrogen by heating, the crystal structure became that of pure palladium again, but an attempt to repeat the cycle failed. This was traced to sulphidation of the surface, the hydrogen used being not quite free from $H_2S$. Other strips showed very little occlusion of carefully purified gaseous hydrogen at room temperature, whether treated immediately after rolling down or after annealing for a few hours at around 800° C. The electrolytic process, however, in which the palladium is made the anode in a weak solution of sulphuric acid, never failed to introduce any desired amount of hydrogen up to saturation. Another process [3] found efficacious was to heat the palladium in a vacuum furnace to about 1100° C for an hour or more, turn off the heating current, and admit gaseous hydrogen when the temperature of the furnace had dropped to about 700° C. This had the disadvantage, however, as compared with the electrolytic method, of not permitting partial saturation. The anomalous result of the first test is now ascribed to the hydrogen sulphide present in the gas which furnished enough atomic hydrogen at the surface during the formation of palladium sulphide to saturate the thin layer of metal underneath.[4] Subsequent attempts failed because of the protecting coating formed by this process.

Wires and strips partially saturated by the electrolytic method gave diffraction patterns in which each line was doubled. The clear space between the lines of each pair shows that crystals of two definite sorts are present, there being few if any crystals with intermediate dimensions. The ratio of intensities varied widely depending upon conditions. In the case of wires about 0.025 cm in diameter, no unsaturated metal lay near enough to the surface to contribute to the photograph if the increase in total resistance amounted to more than 30 per cent, the increase at saturation being nearly 70 per cent. When the saturated surface of partially saturated wires was removed by aqua regia the diffraction pattern due to unaffected metal was relatively intensified, confirming the conclusion that the penetration of hydrogen into the metal is progressive. With partially saturated strips 0.005 cm

[1] In Ångstrom units; to reduce to centimeters multiply by $10^{-8}$.

[2] L. W. McKeehan, PHYS. REV. (2), *20*, 82 (1922).

[3] R. M. Holmes, Science, *56*, 201–202 (1922).

[4] Cf. E. B. Maxted, Chem. Soc., J., *115*, 1050–1055 (1919); *117*, 1280–1288 (1920); *119*, 1280–1284 (1921).

thick the distribution of saturated crystals over the surface of the strip was irregular, as shown by imperfection in the resulting patterns. It is probable that differently oriented crystals become saturated with different facilities.

The smaller parameter obtained from the double patterns showed about the degree of variation usual in crystallometry of a pure metal[1] and was apparently to be ascribed to pure palladium, the range of values being from 3.889 to 3.906. The larger parameter showed a greater variability, ranging from 4.000 to 4.039, which corresponds to a range of 0.24 cm in the position of the line due to reflection from the (531) planes of the lattice, the last lines visible in faint patterns. This range is considerably more than the probable error in measurement. The intensity of reflection was never considerable, however, unless these crystals had parameters in excess of 4.010, and the values for the parameter obtained from intense photographs cluster in the range between 4.023 and 4.039, indicating the existence of a true limiting value somewhere in this range; the value 4.036 is preferred.

An attempt was made to reduce the parameter of saturated crystals by heating them for a short time at 200° C, which treatment reduced the excess resistance in a particular case from 75 per cent, corresponding to slight supersaturation, to 30 per cent. Before heating, the single parameter apparently present was 4.038; after heating the two values 4.025 and 3.900 were obtained, the intensities being roughly the same for the two patterns. Judging by the greater breadth of the lines in the second experiment as compared with those usually observed, the crystals of both sorts were either very small or were badly strained.

An attempt has been made to find places for the hydrogen atoms in the saturated crystals which would at the same time satisfy the observed cubic symmetry and the formula $Pd_2H$ proposed by earlier investigators for a supposed hydride. The process of occlusion would on this basis be analogous to the volume oxidation of calcium crystals, where the introduction of the oxygen atoms actually pulls the metal atoms closer together,[2] and where the process stops definitely at the composition CaO. The low atomic weight of hydrogen makes any such hypothesis regarding its arrangement purely speculative since the proposed structure cannot be checked by intensity measurements. The arrangement already familiar in $Cu_2O$ and $Ag_2O$ is suitable, and, nothing being known about the crystallographic properties of the hypothetical $Pd_2H$ except the facts here recorded, cannot be contradicted. This would place the hydrogen atoms on a body-centered cubic lattice with the same parameter as that

[1] L. W. McKeehan, PHYS. REV. (2), *19*, 537–538; *20*, 424–432 (1922).

[2] A. W. Hull, PHYS. REV. (2), *17*, 42–44 (1921).

here found for the face-centered cubic lattice of palladium atoms, the points of the former lying symmetrically on the trigonal axes (cube body-diagonals) of the latter. This is expressed more formally by stating that palladium atoms occupy the points (0, 0, 0), (0, $a/2$, $a/2$), ($a/2$, 0, $a/2$), ($a/2$, $a/2$, 0) and hydrogen atoms the points ($a/4$, $a/4$, $a/4$), ($3a/4$, $3a/4$, $3a/4$), where $a = 4.036$ is the parameter of a simple cubic lattice. The density of the compound $Pd_2H$ would then be 10.76 gm/cm$^3$, that of Pd being [1] 11.87 gm/cm$^3$. Another possibility is to put both of the two hydrogen atoms absorbed by each face-centered cube of palladium atoms at the centers of opposite faces of one of the eight smaller cubes into which it can be divided. This preserves the identity of the hydrogen molecule as the other arrangement does not, but is less symmetrical, requiring a unit of structure containing 108 palladium atoms and 54 hydrogen atoms to attain cubic symmetry, and is therefore improbable. The variability in the parameter of saturated crystals is against the idea of a definite compound being formed in every case. It is probably only the limit which is approached more or less closely, depending upon the temperature and other factors determining the equilibrium condition.

## Conclusion.

The phenomena here observed seem consistent with the following physical assumptions, some of which have been previously made by others: [2]

1. Palladium and hydrogen are not miscible in all proportions at ordinary temperatures and pressures. Two crystalline phases can coexist, one being practically pure palladium, the other a saturated solution of hydrogen in palladium.

2. The amount of hydrogen in a saturated crystal of palladium, and the distention of the crystal space-lattice thereby, decrease with increase in temperature and with reduction in pressure of dissociated hydrogen in the neighboring space.

3. Unsaturated crystals in conditions favorable to saturation become saturated very rapidly because the introduction of any hydrogen atoms into the interatomic spaces so strains the space-lattice that the entrance of additional hydrogen atoms is facilitated.

4. Saturated crystals are in unstable or metastable equilibrium in air and lose hydrogen by diffusion at a rate which is accelerated by heating. Desaturation once started in any crystal proceeds rapidly to the end because of the intense local strains set up by the removal of a few hydrogen atoms.

[1] L. W. McKeehan, Phys. Rev. (2), *19*, 537–538; *20*, 424–432 (1922).

[2] See appended bibliography.

5. An unsaturated crystal lying too deeply below a surface exposed to atomic hydrogen at ordinary temperatures is unaffected until a considerable part of its bounding surface is covered by saturated crystals, because hydrogen can reach it through neighboring crystals or through intercrystalline amorphous metal by slow diffusion only, and it therefore becomes exposed to hydrogen in quantity only by the opening of pores by expansion of the overlying crystals.

6. The linear resistance-change throughout the greater part of the range of occlusion is due to the varying proportions of the two sorts of crystals which, in consequence of (3) and (4), are the principal constituents of the system. This type of resistance-change is, in fact, a criterion for alloys which are mechanical mixtures of two phases.

7. The small initial rise in resistance and the final slow approach to a limiting value are due to changes in the resistance of intercrystalline material or to defects in intercrystalline contact, or to both.

8. The temporary change in resistance observed when the process of saturation is interrupted [1] is due to the transient presence of partially saturated crystals, the whole mixture simulating the condition of a uniformly dispersed solid solution.

9. Occlusion requires the presence of atomic hydrogen, which may be supplied either by electrolysis at ordinary temperatures or by surface dissociation of gaseous hydrogen at high temperatures.

The appended bibliography may be of service in coördinating the experimental studies in this field in the light of the new crystallographic data.

## THE SYSTEM PALLADIUM-HYDROGEN BIBLIOGRAPHY, 1900–1921.

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RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INCORPORATED.

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# EVAPORATION CHARACTERISTICS OF TUNGSTEN.

By G. R. Fonda.

Abstract.

**Rate of evaporation from tungsten filaments at 2825° K.**—Using the Langmuir method, it was found that *in vacuum* the rate of evaporation per cm² $m$ is independent of the diameter $a$, 1/20 to 1/4 mm, but is over forty per cent greater for fine-grained than for very coarse-grained wires, probably because the evaporation at the boundaries of the crystals is abnormal. *In nitrogen* the rate varied from 2 to 5 per cent of that for the same wire in vacuum, and *in argon* from 1.3 to 3 per cent, increasing as the diameter decreased from 1/4 to 1/15 mm. The variation with size when gas was present is in agreement with the Langmuir theory of heat conduction for hot filaments which supposes that there is around the wire a stationary film of gas through which the evaporated atoms must diffuse. The diameter of the outer surface of this film $b$ varies with $a$ according to the equation: $b \log (b/a) = 0.86$; and this leads to the equation: $ma \log (b/a) = \text{const.}$, with which the experimental results agree. The constants for nitrogen and argon are inversely proportional to the molecular weights.

METHODS of measuring the rate of evaporation of tungsten in the form of filaments have been developed and studied in vacuum by Langmuir.[1] Use of his method in a further study of tungsten filaments in gases as compared with their behavior in vacuum has brought out the extent to which the rate is lowered in nitrogen and argon and also the dependence of the rate on the crystalline structure of the wire.

Drawn wire was used in all cases, both as "thoriated" and as "Non Sag." The former contains 0.6–0.8 per cent thoria and is uniformly and invariably fine grain, so much so that several crystals occur across a diameter of the wire, even in the smallest sizes. The "Non Sag" wire contains less than 0.1 per cent of impurities. In crystallization it varies from a structure as fine grained as the thoriated to one characterized by excessively large and long crystals.

Filaments in 12 cm lengths, mounted in vertical loops, were tested at constant voltage at an initial temperature of 2950° K in the case of the experiments in vacuum, and 2825° K in the case of those in gas. The gas was introduced to the lamp at a pressure cold of 51 cm. The filament temperature was determined by color match on the photometer; only the central portion of the filament was viewed in order to avoid errors from the lower temperature at the portions cooled by the leads. In

[1] Phys. Rev., 2, 329 (1913).

obtaining the final weight of the filament, 1.5 cm next each lead was rejected for the same reason, and, in the case of filaments tested in gas, 1 cm on each side of the tip. Each test was continued to burn-out of the filament and a 7-mm length on each side of the point of burn-out was also rejected, in order to avoid errors due to the molten conditions of the terminals.

## Rate of Evaporation.

The rate of evaporation was determined from Langmuir's equation,

$$m = 2.846 \frac{\sqrt{W_0} - \sqrt{W_f}}{t},$$

where $W_0$ = initial weight in grams per cm,
$W_f$ = final weight in grams per cm,
$t$ = time in seconds.

$m$ is accordingly the rate of evaporation in grams per sq. cm per second.

The results given in Table I. are made up, with the exception of "I." and "II.", from averages from several wires of the same crystalline

### Table I.

*Rate Evaporation of Tungsten Filaments in Vacuum and in Inert Gases.*

| Size Filament. | Character Tungsten. | Crystalline Structure. | Rate of Evaporation gms. per sq. cm per sec. × (10)⁹. | | |
|---|---|---|---|---|---|
| | | | Vacuum. | Nitrogen. | Argon. |
| .051 mm | Non Sag | Large | 300 | — | — |
| " | Non Sag | Small | 420 | 21 | — |
| .069 | Thoriated I. | Small | — | 13 | 9 |
| .076 | Non Sag II. | Large | 270 | 17 | — |
| .102 | Non Sag | Large | 360 | 17 | — |
| " | Non Sag | Segregations | 450 | 16 | — |
| " | Non Sag | Small | 470 | 15 | — |
| " | Thoriated | Small | 440 | 12 | — |
| .127 | Non Sag | Large | 170 | 8 | — |
| " | Non Sag | Small | 330 | 11 | — |
| " | Non Sag II. | Small | 400 | 12 | — |
| " | Thoriated | Small | 350 | 14 | — |
| " | Thoriated I. | Small | — | 10 | 6 |
| .254 | Non Sag II. | Small | 350 | 8 | — |
| " | Thoriated I. | Small | — | 6 | 4 |

character. "I." and "II." denote individual wires drawn to different sizes. By a structure of "small" crystals is meant an aggregation of crystals whose width is less than that of the wire. The designation "large" crystals refers to those whose length is greater than several diameters of the wire, varying in fact from 0.4 mm to 10 mm long.

"Segregation" refers to a wire having long crystals separated by segregations of small ones. From 6 to 18 tests were made on each wire. By the help of Langmuir's curves for the variation in rate of evaporation with temperature, and for the sake of a direct comparison, the rate of evaporation is expressed throughout in terms of its value at the constant temperature of 2825° K.

It is noticeable that the rate in both vacuum and in gas tends to increase with increase in the number of grain boundaries. This is in accord with results obtained by Rosenhain and Ewen,[1] in the case of silver, copper and zinc, for differences in crystalline size, and the explanation would seem to lie in the presence of larger amounts of a more volatile phase in small grain metals, as suggested by those authors. If one assumes with them the presence of amorphous tungsten between the grains, then there will be present in the wire two phases of differing vapor pressure; for the amorphous one, like all undercooled liquids, must have a higher vapor pressure than the crystalline. If the intergranular material is made up rather of insoluble impurities, then in general these also will have a higher vapor pressure. In fact pronounced channels develop between the grains as the filaments are burned, illustrating the abnormal evaporation that takes place at the boundaries.

It is noticeable also for wires of the same crystalline character that the evaporation per unit area in vacuum is approximately the same independent of the diameter, and is therefore purely a function of the exposed surface. In a gas, however, a decided influence is exerted by the wire diameter.

It is true that the rates of evaporation in gas are decidedly lower than those in vacuum, but the extent to which they are lowered varies with the diameter of the wire. In nitrogen, for instance, the rate for the largest wire of 0.254 mm diameter is only 2 per cent of that for the same wire in vacuum, but it rises to 6 per cent for the smaller wire of 0.069 mm diameter. In argon the rate is still lower, but again the same dependence on diameter is shown, the range this time lying between 1.3 and 3.9 per cent of the rate in vacuum for diameters of 0.254 and .069 mm respectively.

Incidentally it should be noticed that the ratio between the rates in argon and in nitrogen is 0.69, 0.60, and 0.67, for three different sizes of wire; and that this fairly constant value is approximately the same as the inverse ratio of their molecular weights, 0.70.

The dependence of the rate of evaporation on wire diameter in gas and not in vacuum is of particular interest, and an explanation for it has

[1] J. Inst. Metals, 8, 149–170, 1912.

been found in the diffusion phenomena which take place in gas, as suggested by the relationship between the rate and the molecular weight of the gas. In vacuum an atom of tungsten, on evaporation from the filament, proceeds in an unimpeded path to the bulb, so that the diameter of the filament should in fact have no effect on the rate.

For the experiments in gas Dr. Langmuir made the suggestion that the same phenomenon was involved as described by him for the heat loss from a wire in a gas [1] and calculation on this assumption proved to give very good agreement. His theory calls for a relatively stationary film of gas of definite diameter about a wire, through which the heat is conducted away from the filament. Outside of this film another distinct zone occurs in which the heat is carried away by convection currents. The application to the present work lay in the hypothesis that tungsten atoms evaporating from a filament in a gas should obey the same law of diffusion while within this stationary film of gas, free to return to the filament as well as to move to the outer edge of the film from which they would be carried to the bulb by convection currents of gas. Their actual evaporation then would depend on the balance between these two courses of diffusion and would be determined by the factor $\log b/a$, where $a$ is the diameter of the filament, and $b$ that of the gas film.

This is seen by examination of Langmuir's equation for heat loss

$$W = \frac{2\pi l}{\log b/a}(\phi_2 - \phi_1)$$

or, for unit length of filament at constant temperature in the same gas,

$$W = \frac{\text{const.}}{\log b/a}.$$

The rate of evaporation, $m$, is in terms of grams per sq. cm. When expressed in the same units as the heat loss, grams per unit length of filament, it becomes proportional to $ma$. If the thickness of the film of gas determines both the heat loss and the rate of evaporation, then $ma$ should be proportional to $W$, and the condition should hold

$$ma \log b/a = \text{const.}$$

In Table II. the diameter of this film is calculated for the different sizes of wire from Langmuir's equation $\log b/a = 2B/b$. $B$ is the thickness of the film over a plane surface, and the same value of 0.43 cm is used here as for heat conduction in nitrogen. The product $ma \log b/a$ is given at the end of the table for three different cases, each dealing with fila-

[1] PHYS. REV., 34, 410 (1912).

ments from the same wire drawn to different sizes. The first two cases are for the same wire in argon and in nitrogen, and the third case is for a different wire in nitrogen.

TABLE II.

| Filament Diameter $a$, cm. | Diameter Gas Film $b$, cm. | log $b/a$. | $m(10)^9$. | | | $ma \log b/a(10)^{11}$. | | |
|---|---|---|---|---|---|---|---|---|
| | | | I($A$). | I($N$). | II($N$). | I($A$). | I($N$). | II($N$). |
| 0.0069 | 0.241 | 3.57 | 9 | 13 | — | 22 | 32 | — |
| .0076 | .246 | 3.50 | — | — | 17 | — | — | 45 |
| .0123 | .276 | 3.11 | 6 | 10 | 12 | 23 | 38 | 46 |
| .0254 | .333 | 2.58 | 4 | 6 | 8 | 26 | 39 | 52 |

With each wire the product shows a satisfactory constancy for the different sizes, so that this hypothesis for the mechanism of evaporation of a filament in a gas seems a perfectly reasonable one. This is particularly so as the thickness of gas film necessary to assume as basis for this hypothesis is the same as already developed in explanation of the heat conduction from wires in gases.

I desire to express to Dr. Langmuir my gratitude for his interest and suggestions.

RESEARCH LABORATORY,
GENERAL ELECTRIC COMPANY,
SCHENECTADY, N. Y.,
October 15, 1922.

# THE REVERSIBLE INDUCTIVITY OF ROCHELLE SALT CRYSTALS AND ITS RELATION TO FREQUENCY AND TEMPERATURE.

By John G. Frayne.

Abstract.

**Reversible inductivity of Rochelle salt crystals** is defined as $k_r = -dD/dE$ or the limit of the ratio of the change of induction to the change of electric field in the dielectric as these approach zero. *The method of measurement* used involved determining the capacity of a condenser with a plate of Rochelle salt crystal, cut normal to the ă-axis, as dielectric, by adjusting the oscillating circuit containing it to resonance with a loosely coupled vacuum tube circuit. *Variation with frequency of alternating field* was studied up to $4 \times 10^7$ cycles, for the crystal at 0° C (Fig. 3). Above the natural periods of vibration of the plate, 60,000 and 156,000 cycles, $k_r$ was constant at 70, while below them it was constant at about 112 to 8,000 cycles and then began increasing. The lower frequency values are affected by piezo-electric effects due to mechanical vibration in certain ranges and by polarization effects which increase as the frequency decreases; hence the high frequency values have a simpler physical significance. *Variation with temperature, − 80° to 50° C:* Curves obtained for frequencies of $10^6$, 50,000 (near resonance), and 8,000 cycles (Fig. 4), all show maxima for about − 16° and 24° C. The minimum at about 6° may be associated with the maximum piezo-effect which occurs in this range. *Hysteresis loop:* The previous results are for an applied electric field of zero. As the field is increased, $k_r$ reaches a maximum, then a minimum, then increases to infinity as conduction begins for 2,700 or 3,000 volts/cm, depending on the direction. *Natural polarization* may be estimated from the asymmetry of the hysteresis loop. Two samples gave 125 and 175 volts/cm. A comparison of the temperature curves for three samples cut from the same crystal shows marked differences which indicate that the natural polarization is far from uniform even in the same crystal. *Relation of $k_r$ to high frequency resistance* is probably close. The two properties vary in general in much the same way. This seems to indicate that the energy absorbed in the dielectric is very simply related to the process of doublet formation.

**Mechanical vibrations of Rochelle salt condenser in oscillating circuit.**— At the natural frequencies of the crystal plate, abnormal values of $k_r$ and of the resistance were found. In the case of the transverse resonance, the computed wave-length was four times the width of the plate.

IN a paper on the theory of ferromagnetism in 1908 R. Gans[1] introduced a quantity which he called the reversible permeability of iron. The name was suggested to him by the fact that iron can be taken through a reversible hysteresis cycle, provided the field intensity is varied at the start in a direction *opposite* to the existing field in the

[1] R. Gans, Annalen der Physik, 27, pp. 1–6, 1908.

iron. The resulting loop may be made as small as desired, and Gans defines the limiting value of the ratio of the change in the induction to the change in the field strength as the *reversible permeability* of iron.

When an alternating field is applied to iron the induction undergoes a hysteretic cycle for each current cycle, and if the alternating field be made very small, the ratio of the maximum amplitude of the induction per cycle to the maximum amplitude of the field strength per cycle will become the reversible permeability of Gans. By measuring the self-induction of an iron core solenoid in a resonating circuit Fritz Erhardt [1] has measured the reversible permeability under various conditions.

In a recent paper Valasek [2] has shown that the behavior of Rochelle salt crystals in an electric field is analogous to that of iron in a magnetic field. He found that a marked dielectric hysteresis loop existed when a Rochelle salt crystal was carried through a cycle of electric field intensities. The dielectric constant of this substance, consequently, depends on the field strength when measured by direct or alternating current methods.

Carrying the analogy further I have denoted by the term "*reversible inductivity*" the quantity which corresponds to reversible permeability in ferromagnetic substances. If we take a point on the normal induction curve (Fig. 1) of a sample plate of Rochelle salt and gradually decrease

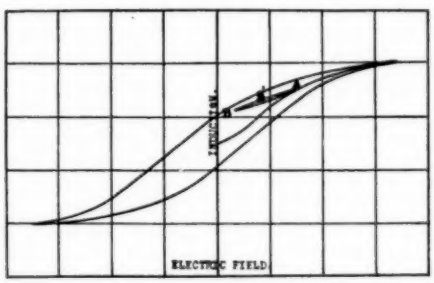


Fig. 1.

the field to $B$, then reverse the direction of the field, the point $A$ will again be reached. If the field had only been reduced to $B'$ and increased again to $A$, the area of the loop would have been reduced, and in the limiting case $AB$ will become a straight line. The value of

$$\text{limit } (\Delta E \doteq 0) \; -\frac{\Delta D}{\Delta E} = -\frac{dD}{dE} = k_r,$$

which we shall call the reversible inductivity.

[1] Fritz Erhardt, Ann. der Phys., 54, p. 41, 1917.

[2] J. Valasek, PHYS. REV., 4, p. 475, 1921.

The piezo-electric activity of Rochelle salt crystals tends further to complicate the dielectric properties of the substance when studied from the resonance standpoint. Cady [1] has shown that the dielectric constant of quartz, another piezo-electrically active substance, changes very abruptly when the period of the exciting field approaches the natural period of vibration of the crystal plate. The counter piezo-electromotive force produces a displacement in the dielectric which becomes very large at resonance, and being practically 180° out of phase with the applied e.m.f. makes the actual displacement negative over a narrow band of frequencies at the resonance point.

Valasek [2] has shown that the piezo-electric properties and dielectric constant of Rochelle salt are markedly dependent on temperature, the piezo response rising to a maximum between − 20° C and + 20° C, but dropping sharply to zero below and above these temperatures. He also found that the dielectric constant when measured by direct current methods increased rapidly between the same temperatures.

In this paper I have studied the effect on the dielectric constant of changing the frequency of the exciting field from 1,000 cycles to $4 \times 10^7$ cycles per second. At the same time the temperature-inductivity graphs have been plotted for different frequencies. Curves have also been obtained showing how the inductivity depends on the state of polarization of the crystal plate, and finally the properties of different plates cut from the same crystal have been examined.

## Experimental Procedure.

The crystal plate which formed the dielectric of the condenser used in this research was cut so that its face was perpendicular to the ă-axis, so as to obtain the greatest piezo-electric effect. Tin foil was fastened with shellac to either side, and leads were brought out from the foil through the stopper of the glass tube in which the condenser was contained. Phosphorous pentoxide was always inserted in the bottom of the tube while the condenser was in use, in order to keep the sides of the plate free from moisture. The glass tube itself was placed in a Dewar flask, and the temperature of the plate was usually kept at 0° C, except when temperature variation was desired. Arrangements were also made, see Fig. 2, for applying a steady electric field to the crystal, the size and direction of the latter being capable of adjustment.

The capacity of the condenser gives immediately the value of the dielectric constant, and when a weak alternating field is used the value

[1] Cady, P. I. R. E., 10, p. 83, 1922.
[2] Valasek, Phys. Rev., 19, p. 478, 1922.

obtained for this constant coincides with the reversible inductivity of the material under the conditions in question.

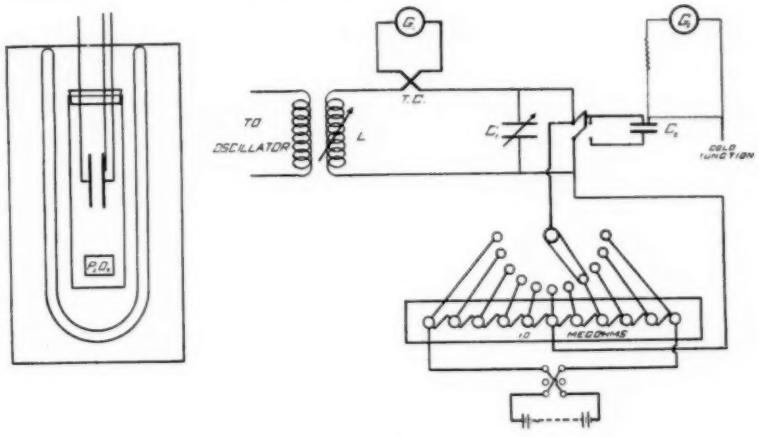


Fig. 2.

A vacuum tube was used as a source of undamped oscillations, and frequencies from a few thousand to 40,000,000 cycles a second were obtained. The oscillator was very loosely coupled to the receiving circuit, the coils being placed about a meter apart. With the plate condenser out of the circuit the variable capacity $C$ was adjusted for resonance, the latter being indicated by the maximum deflection of the galvanometer $G$ connected to the vacuum thermo-couple which was inserted in the resonating circuit. The crystal plate condenser was then inserted in parallel with $C$ and the latter adjusted again for resonance. The capacity and effective resistance of the crystal plate condenser were then calculated as follows:

Let $C_x$ = capacity of plate condenser.
$R_x$ = H.F. resistance of plate condenser.
$C_1$ = capacity of $C$ at first resonance.
$C_2$ = capacity of $C$ at second resonance.
$L_1$ = inductance of coil $L$.
$I_1$ = current through $C$.
$I_2$ = current through $C_x$.

From first resonance condition, if the mutual inductance between oscillator and receiving circuit be neglected, $LC_1 = \omega^2$, $\omega$ being $2\pi\times$ the frequency. In order to write an analytical statement of the second condition for resonance, it is necessary to find an expression for the vector impedance of two condensers in parallel, one of which has an

equivalent series resistance. If we denote by $E$ the instantaneous e.m.f. across the condensers, then

$$I_1 = E \Big/ \frac{j}{C_2\omega},$$

$j$ being $\sqrt{-1}$,

$$I_2 = E \Big/ \left( R_x + \frac{j}{C_x\omega} \right) = \frac{E(R_x - j/C_x\omega)}{R_x^2 + 1/C_x^2\omega^2}.$$

The total current is therefore

$$I = I_1 + I_2 = E \left\{ \frac{R_x}{R_x^2 + 1/C_x^2\omega^2} - j\left( C_2 + \frac{C_x}{R_x^2C_x^2\omega^2 + 1} \right) \right\} \quad (1)$$
$$= E(A - jB)$$

or

$$I = E \Big/ \left\{ \frac{A + jB}{A^2 + B^2} \right\}.$$

Hence the impedance of the divided circuit is

$$\frac{A}{A^2 + B^2} + j\frac{B}{A^2 + B^2}.$$

The impedance of the entire resonant circuit is, therefore,

$$-jL\omega + A/(A^2 + B^2) + jB/(A^2 + B^2).$$

The condition for resonance is that the coefficient of $j$ becomes zero. Hence

$$L\omega = B/(A^2 + B^2).$$

As a first assumption, which is supported by experiment, we shall neglect $A^2$ in comparison with $B^2$. Then $L\omega = 1/B$ or

$$\omega^2 = \frac{1}{L\{C_2 + C_x/(R_x^2C_x^2\omega^2 + 1)\}}. \quad (2)$$

As a second assumption, if we consider $R_x^2C_x^2\omega^2$ negligible in comparison to unity, then

$$\omega^2 = \frac{1}{L(C_x + C)},$$

which is the ordinary condition for resonance. From (2) we obtain

$$C_x = (C_1 - C_2)(R_x^2C_x^2\omega^2 + 1).$$

From this relation $C_x$ can be determined, provided $R_x$ is known. The latter can best be found by inserting the plate condenser in series with the air condenser and noting the resonance deflections before and after

insertion. The value of $R_x$ can very easily be calculated from these observations. Except at very high freuqencies, or near the natural period of the crystal where the absorption of energy becomes very large, $R_x^2 C_x^2 \omega^2$ is very small compared to unity, and we may, with a fair degree of accuracy, write $C_x = C_1 - C_2$ which is the ordinary law for adding capacities in parallel.

The coil $L$ was gradually decreased by taking off turns of wire as the frequency of the field was increased. When the frequency reached $4 \times 10^7$ cycles per second, the coil consisted of only one turn. In order to get accurate results at this frequency, all the connecting wires were made as short as possible, thereby reducing their inductance to a negligible quantity.

In order to measure $k_r$ it was necessary to use very weak alternating fields, and in no instance did the alternating field in the dielectric exceed 3 volts per cm. It was found by trial that a variation from .5 to 5.0 volts per cm produced no measurable change in $k_r$. Above 5 volts $k_r$ increased with increasing field strength up to about 100 volts per cm. Of course, the quantity as measured at these high field strengths is no longer the reversible inductivity of the substance.

## Frequency Variation.

The first thing of interest in studying reversible inductivity is the effect of changing the frequency of the exciting field. In the method used by Valasek for determining the statical dielectric constant, he measured the charge on the condenser by the throw of a ballistic galvanometer, but it is doubtful if the value he obtained in that manner really represents the true dielectric constant. The hysteresis property of the substance would indicate that a considerable time would elapse before the condenser was really discharged, it being well known that Rochelle salt crystals retain their polarization for some time after the field has been removed. On the other hand when an alternating field is used, provided the alternations are sufficiently rapid, it is conceivable that the material would scarcely have sufficient time to become polarized in any one direction. The curve in Fig. 3 shows that as the frequency

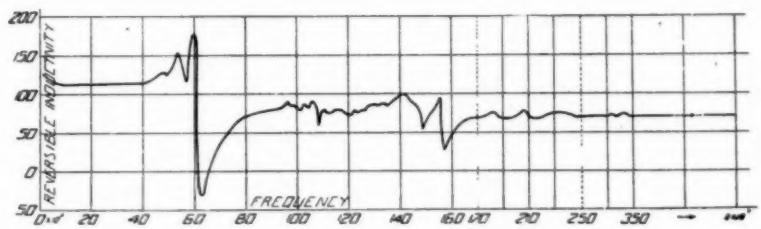


Fig. 3.

is increased above zero $k_r$ drops until a frequency of about 8,000 cycles per sec. is reached. From this frequency up to about 50,000 cycles per sec. very little change is apparent. However, at 61,000 cycles per sec. the natural longitudinal period of vibration is reached, and the dielectric constant becomes negative over a narrow range of frequencies. Just below and above this frequency the absorption of energy by the plate is very pronounced, the effective resistance becoming about several thousand ohms. Between 80,000 and 140,000 cycles per sec. the curve shows irregularities which are probably due to harmonics of the natural vibration or interference between the latter and sub-harmonics of the higher resonance vibration. At 156,000 cycles per sec. another resonance point is reached, but the changes in the inductivity here are small compared with the previous values. Between 170,000 and 350,000 cycles per sec. a few small variations are found which are probably due to excitation of the crystal by frequencies bearing a relation to the natural period of vibration.

If we take Young's Modulus for the substance as $4 \times 10^{11}$ dynes per $cm^2$ and the specific gravity as 1.76 grams per c.c., the velocity of sound in the crystal is given by $v = \sqrt{M/\rho} = 4.77 \times 10^5$ cms per sec. The wave-lengths corresponding to the resonance frequencies above are respectively 7.70 and 3.30 cms. From the manner in which the plate is mounted the transverse vibration should be the greatest, and the greatest changes in the inductivity would be expected there. If the plate were vibrating freely the wave-length should be twice the breadth of the plate, but it is actually four times the breadth. The wave-length of the longitudinal vibration is no multiple of the length 2.34 cm, and this is probably caused by the mounting which tends to damp the longitudinal vibrations.

Above 350,000 cycles per sec. the value of $k_r$ remained constant up to $4 \times 10^7$ cycles per sec. which was the maximum frequency used. The constancy of the inductivity over such a large range of frequency would seem to indicate that this value of 70 is correct for this specimen of the salt. Below the resonance point the inductivity may be influenced by polarization effects or the proximity of the resonance vibrations. At frequencies of ten million cycles or more, however, it is difficult to conceive of permanent polarization effects. As it was experimentally difficult to use a resonance method at frequencies above $4 \times 10^7$, further investigation above this frequency has been left over until a better method has been found for this purpose.

The high frequency resistance remained constant with $k_r$. At the resonance points, as stated above, the absorption increased before and after the natural periods of vibration of the plate. At frequencies

approaching zero the resistance increased in about the same ratio as the inductivity.

### Temperature Variation.

The curves in Fig. 4 show that it would be impossible to work with Rochelle salt at room temperatures and obtain any consistent results. Hence the measurements carried out in the last section were all carried out at 0° C, the tube containing the Rochelle salt being entirely surrounded by melting ice. It will be noticed that all the temperature inductivity curves show the same characteristics. The value of $k_r$ rises from about 12 at − 80° C to 100 or more, depending on the frequency, in the neighborhood of − 16° C. Then it takes a sharp dip dropping by about 50 per cent at + 6° C. Here it rises to a sharp maximum at about 24° C, where it starts to drop again. The temperature was not carried above 50° C, as the substance melts at about 51° C. The curve *A* represents conditions from the highest frequency used down to the resonance region. The curve *B* represents conditions at a frequency of 50,000 cycles per sec., where Fig. 3 indicates a large value of $k_r$ at zero Centigrade. It is peculiar that throughout the entire range of temperature, the values of $k_{r_1}$ in *B* are greater than at the corresponding temperatures in *A*. The same condition holds good in *C* which represents conditions below resonance and above 8,000 cycles per sec.

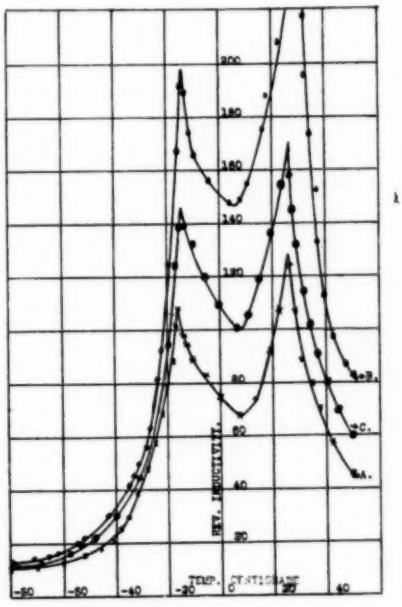

Fig. 4.

The temperature inductivity curves, by dropping to a minimum at + 6° C, vary in exactly the opposite manner to the values of the dielectric constant as determined by Valasek [1] using the ballistic galvanometer method. He did, however, find that the piezo-electric response reached a maximum at about 0° C, rising from practically nothing at − 20° C and descending sharply again at + 23° C. The stresses that are set up in the crystal due to the alternating field produce a counter piezo-electromotive force, which in turn produces a displacement which may be almost

[1] Loc. cit.

180° out of phase with the displacement caused by the exciting field. Hence in a region where the piezo-response is a maximum, we might expect a maximum counter displacement in the dielectric and this will in turn cause a diminution in $k_r$ at that place.

Below − 16° C and above + 24° C the curves are of interest in that we have a sharp variation of $k_r$ with temperature. These regions lie outside the piezo-electric range of activity, and the effect of temperature seems to increase or decrease the polarization depending on the particular part of the temperature range in question. An increase in the polarization is connected very closely with an increase in the high frequency resistance. This seems to indicate that the energy absorbed in the dielectric is very simply related to the process of doublet formation. High frequency resistance, as a rule, has no counterpart in direct current measurements, owing its existence to the dissipation of electrical energy in the dielectric, as the latter charges and discharges with the alteration of the field. It is quite natural, then, to expect a large high frequency resistance to accompany a large polarization on account of the energy required to separate the electric doublets. I have avoided using the term high frequency conductivity altogether, as it could at best be defined as the reciprocal of the high frequency resistance. The latter, as we have seen, has a physical significance, but we can only attach an indirect meaning to the former.

## Effect of Electrostatic Field.

As $k_r$ is defined as limit $(\Delta E \doteq 0) - \frac{\Delta D}{\Delta E}$, it will be seen that if the crystal be acted on by an electrostatic field, the value of $k_r$ will in general depend on the value of $E$ and the previous history of the electric field in the crystal. In fact $k_r$ will very nearly be the slope of the $D, E$ curve for any given value of $E$. In order to measure the value of $k_r$ as suggested above the crystal was carried through a regular hysteresis cycle in the manner described by Valasek.[1] At several points on the normal induction curve, as well as on the hysteresis loop proper, the inductivity was determined as before, and the results obtained for two different plates are shown in Figs. 5 and 6. The dotted line (Fig. 5) shows how $k_r$ varies with increasing field. It first reaches a maximum and then gradually declines until a field strength of 2,200 volts per cm is reached where it begins to increase again. When the field reaches a value of 2,750 volts per cm the crystal begins to conduct, the capacity approaching infinity. The field is then gradually decreased and the capacity reaches a maximum slightly above

[1] Loc. cit.

zero field. Below zero field it gradually decreases down to the largest negative field used. On increasing the field again towards zero the capacity increases in a rather irregular fashion up to a maximum for a

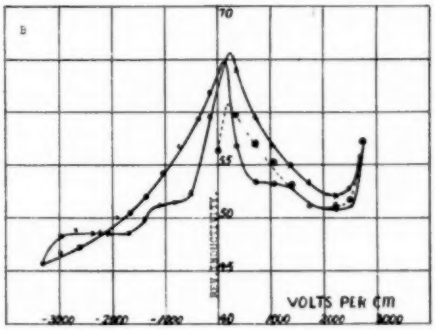


Fig. 5.

positive field of 250 volts per cm. For higher field strengths the capacity gradually decreases until the region of conductivity is reached, where it again starts to ascend. Fig. 6 shows a similar curve for another plate of the material, the normal induction curve being obtained this time by applying the electric field in the opposite direction along the ă-axis. The condenser became conducting after the field had been reversed and had reached a value of slightly over 3,000 volts per cm. At 3,800 volts per cm the capacity was increasing indefinitely.

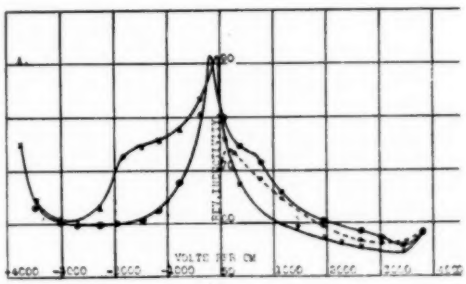

Fig. 6.

The increasing inductivity and conductivity occurring only in one direction of the electric field can be explained by the natural polarization of the crystal along the ă-axis. This natural electric field adds on to the external field in one direction and weakens it in the other direction. Hence the dielectric will break down in one direction for a smaller field than it will in the opposite direction. If there were no natural polariza-

tion the two maxima would be equally distant on either side of the axis. Hence the distance along the abscissæ out to the ordinate bisecting the distance between the maxima will give a measure of the natural field. For one plate the value is 125 and for the other 175 volts per cm.

## Non-uniformity in Crystal.

In the last section the behavior of two different crystals was discussed and a glance at the curves will show a great difference in their characteristics. In Fig. 7 three inductivity-temperature curves are shown

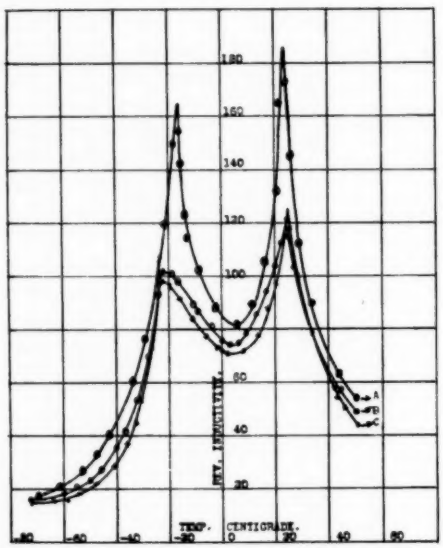


Fig. 7.

for three different plates. The frequency used was the same for the three plates, namely, two million cycles per sec. This frequency was sufficiently removed from the natural periods of any of the samples, so that effects due to different linear dimensions could be neglected. Two of the samples show very similar relations, but the third is radically different in that it reaches much higher maximum values and also has a higher value at 0° C than either of the other two. As these samples were cut from the same crystal and were used under exactly the same conditions we must attribute these results to the lack of uniformity in the crystal so far as the natural polarization is concerned.

In this paper I have not dealt with frequencies above $4 \times 10^7$ cycles per second. The resonance method used here is not very applicable to higher frequencies, but other methods are possible whereby the dielectric

constant can be measured for wave-lengths down to one cm. As the natural periods of the doublets lie somewhere in the limiting radio frequency range, experimentation in this region ought to be very fruitful. The fact that the value of $k_r$ remained constant up to the limiting frequency used implies that the grouping of doublets in micro-crystals apparently does not exist. In the case of reversible permeability measurements made on iron, resonance values were found in the neighborhood of 10 million cycles per second, in addition to the resonance values directly traceable to molecular vibrations at frequencies of about $10^{10}$ cycles per second.

I wish to express my thanks to Dr. W. F. G. Swann for his active interest in this research and to Dr. J. A. Valasek for his kindness in putting crystals and crystal-cutting apparatus at my disposal.

UNIVERSITY OF MINNESOTA,
September 16, 1922.

# A GENERALIZATION OF BIOT–SAVART'S LAW.

By Hillel Poritsky.

Abstract.

**Magnetic field due to an element of current.**—*Any generalization of the Biot-Savart law* differs from it by the addition of a "null"-field, that is, a field that vanishes when evaluated for a closed circuit. It is demonstrated in two ways that all null-fields are fields due to doublets coinciding with the elements of current, whose poles act with an arbitrary law of force. Since at each point the null-field is perpendicular to the Biot-Savart field, adding a null-field to the Biot-Savart law will only complicate it. This idea of null-fields may be extended to closed surfaces and generalized to higher dimensions. No experiment could detect such null-fields if they exist.

SHORTLY after Oersted's discovery of the deflection of a magnetic needle in the neighborhood of a current-bearing wire, the well-known Biot-Savart law was proposed resolving the magnetic field of currents into a sum of infinitesimal fields, each due to an element of current. It is proposed to find the most general elementary field that could be used to account for experimentally observed magnetic fields. Such a generalization (to the writer's knowledge, at least) has not been worked out. It will be shown that the elementary fields by which the Biot-Savart field could be replaced are arbitrary to within one arbitrary function of a variable, but are all essentially more complicated.

Since electricity flows only in closed circuits, it is obvious that we may add to the field which Biot-Savart's law ascribes to an element of current an elementary field $F$, such that the effects of $F$, when summed for a closed circuit, will vanish. We may term $F$ a "null"-field. Conversely, any two elementary fields that upon integration for a closed circuit yield the same (experimentally observed) field differ by a "null"-field. The problem is therefore reduced to finding all possible "null"-fields.[1]

That "null"-fields exist is obvious from a few simple examples. Consider, indeed, the field due to a magnetic doublet coinciding with the element of current. When a closed curve is lined with such doublets the total effect is nil. An even simpler example is a field in which the intensity is everywhere equal and parallel to the element of current.

All elementary fields considered will be assumed to be proportional to the product of the current $i$ and the length of the element, and to

[1] Such elementary fields are mentioned at least by A. G. Webster in his Theory of El. and Mag., p. 422, but are not determined there.

possess symmetry about the line bearing the element of current, more precisely, to remain invariant under rotations about that line. In what follows we will assume $i = 1$, and refer to an element of current through the infinitesimal vector with which it coincides.

Choose a closed circuit consisting of three elements of current $\boldsymbol{r}$, $\boldsymbol{s}$, $\boldsymbol{t}$, in the form of a small triangle situated near the point $P$, and consider the field due to it at a certain point $O$. Denote by $\boldsymbol{F}(\boldsymbol{u})$ the field produced at $O$ by an element of current $\boldsymbol{u}$ situated near $P$. $\boldsymbol{F}$ is therefore a vector function of its vector argument $\boldsymbol{u}$. Then, since $\boldsymbol{r}$, $\boldsymbol{s}$, $\boldsymbol{t}$ form a closed circuit, that is

$$\boldsymbol{r} + \boldsymbol{s} + \boldsymbol{t} = 0,$$

the field caused by all three of them at $O$ vanishes, or

$$\boldsymbol{F}(\boldsymbol{r}) + \boldsymbol{F}(\boldsymbol{s}) + \boldsymbol{F}(\boldsymbol{t}) = 0.$$

Transposing,

$$-\boldsymbol{t} = \boldsymbol{r} + \boldsymbol{s},$$

and

$$-\boldsymbol{F}(\boldsymbol{t}) = \boldsymbol{F}(\boldsymbol{r}) + \boldsymbol{F}(\boldsymbol{s}).$$

Since $\boldsymbol{t}$, $-\boldsymbol{t}$ in themselves are a closed circuit, $\boldsymbol{F}(-\boldsymbol{t}) + \boldsymbol{F}(\boldsymbol{t}) = 0$, so that

$$-\boldsymbol{F}(\boldsymbol{t}) = \boldsymbol{F}(-\boldsymbol{t}) = \boldsymbol{F}(\boldsymbol{r} + \boldsymbol{s}),$$
$$\boldsymbol{F}(\boldsymbol{r} + \boldsymbol{s}) = \boldsymbol{F}(\boldsymbol{r}) + \boldsymbol{F}(\boldsymbol{s}).$$

In other words, $\boldsymbol{F}$ for the resultant of two vectors is the sum of $\boldsymbol{F}$ for the two vectors separately. $\boldsymbol{F}$ is therefore a linear vector function. It is determined when given for three non-coplanar vectors, thus involving nine arbitrary constants. Considerations of symmetry, however, limit the number of constants to two.

Indeed, we may resolve any infinitesimal vector at $P$ into $\boldsymbol{u}$ along the line $OP$ and $\boldsymbol{v}$ perpendicular to it. Since a rotation about $OP$ leaves $\boldsymbol{u}$ and therefore $\boldsymbol{F}(\boldsymbol{u})$ unchanged, $\boldsymbol{F}(\boldsymbol{u})$ must be directed along $\boldsymbol{u}$, so that

$$\boldsymbol{F}(\boldsymbol{u}) = f\boldsymbol{u},$$

where $f$ is a constant. As to $\boldsymbol{F}(\boldsymbol{v})$, it must be perpendicular to $OP$. For, if we carry out a rotation about $OP$ of 180°, $\boldsymbol{v}$ becomes $-\boldsymbol{v}$. $\boldsymbol{F}(\boldsymbol{v})$ and the vector into which it goes, which is $\boldsymbol{F}(-\boldsymbol{v})$, lie in the same plane and form equal angles with $OP$. Their sum cannot vanish unless they are perpendicular to $OP$. Moreover, $\boldsymbol{F}(\boldsymbol{v})$ must also lie in the plane determined by $OP$ and $\boldsymbol{v}$. If $\boldsymbol{F}(\boldsymbol{v})$ lay outside that plane, imagine in it current flowing in a circle having $O$ for its center and passing through $P$. Revolving $\boldsymbol{v}$, $\boldsymbol{F}(\boldsymbol{v})$ about the axis of the circle we obtain the field due to every element of the circle. All the intensities lie on a cone,

and will have a non-vanishing resultant along its axis, unless the cone reduces to a plane. Therefore, $\boldsymbol{F}(\boldsymbol{v})$ is directed along $\boldsymbol{v}$.

$$\boldsymbol{F}(\boldsymbol{v}) = g\boldsymbol{v},$$

where $g$ is a constant.

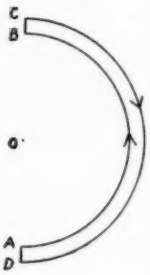


Fig. 1.

The two constants $f$, $g$ become $f(r)$, $g(r)$, functions of the distance $r = OP$, once we let $O$ and $P$ wander about in space. To find out how they vary with $r$, consider a plane circuit $ABCD$ indicated in the figure, consisting of two concentric semi-circles $AB$, $CD$ of radii $r$, $r + dr$ respectively, with center at $O$ joined by segments $BC$, $DA$ of length $dr$ each, with the current flowing in the direction of the arrows. Let $\boldsymbol{R}$ be the vector from $O$ to any point on the circuit. While $\boldsymbol{R}$ is on the semi-circle $AB$, $d\boldsymbol{R}$ is perpendicular to $\boldsymbol{R}$ giving the contribution $g(r)d\boldsymbol{R}$ to the field at $O$. The field due to the current flowing around the inside semi-circle $AB$ is therefore

$$\int_A^B g(r)d\boldsymbol{R},$$

the integration being carried out along the semi-circular path. Since $r$, and consequently the integrand $g(r)$, are constant

$$\int_A^B g(r)d\boldsymbol{R} = g(r)\int_A^B d\boldsymbol{R} = g(r)\cdot\vec{AB}.$$

Similarly, the outside semi-circular current $CD$ gives rise to the field

$$g(r + dr)\cdot\vec{CD}.$$

As to the elements of current $BC$, $DA$ that complete the circuit, they point in the direction of $\boldsymbol{R}$, and against it, respectively, and yield $BC\cdot f(r)$ in the direction $OB$, and $-DA\cdot f(r)$ in the direction $OA$. Thus, the magnetic intensities due to the four parts of the closed current are all directed along the diameter $DAOBC$. Their resultant is zero, if the sum of their magnitudes vanishes. That leads to the equation

$$2rg(r) - 2(r + dr)g(r + dr) + 2f(r)dr = 0$$

or

$$\frac{d[rg(r)]}{dr} = f(r).$$

This condition is also sufficient. Indeed, let $\boldsymbol{R}$ be directed from $O$ to any closed current flowing along the curve $C$. Put $\boldsymbol{R} = r\boldsymbol{U}$ where $\boldsymbol{U}$

is a unit vector along $\boldsymbol{R}$, and $r$ is its length. Then

$$d\boldsymbol{R} = rd\boldsymbol{U} + \boldsymbol{U}dr,$$

$d\boldsymbol{R}$ thus being broken into components perpendicular to $\boldsymbol{R}$ and along it. The field due to $d\boldsymbol{R}$ is therefore

$$g(r)rd\boldsymbol{U} + f(r)\boldsymbol{U}dr;$$

and making use of

$$f(r)dr = d[rg(r)],$$

we may write the field due to $d\boldsymbol{R}$ in the form

$$rg(r)d\boldsymbol{U} + \boldsymbol{U}d[rg(r)] = d[rg(r)\boldsymbol{U}].$$

If we integrate along the curve $C$ from $A$ to $B$, we therefore get

$$\int_A^B d[rg(r)\boldsymbol{U}] = [rg(r)\boldsymbol{U}]_A^B.$$

Now, if $\boldsymbol{R}$ runs all around the curve, $B$ coincides with $A$ and we get a zero field.

The expression $[rg(r)\boldsymbol{U}]_A^B$ for the field due to the open circuit $AB$ lends itself to an interesting interpretation. The vector it yields will be obtained for the field at $O$ if we placed a pole at $B$ acting radially with a force $rg(r)$, and a pole acting with a force—$rg(r)$at $A$. We may choose $rg(r)$ arbitrarily, $f(r)$ being then determined by differentiation. Letting $A$, $B$ be close to each other and form the end points of an element of current we get the result: *The most general "null"-field, or field due to an element of current that will evaluate to zero when summed for a closed circuit, is the field due to a doublet coinciding with the element of current, whose poles act radially with an arbitrary law of force.*

This result could also be established in a much simpler manner as follows. If two points $A$, $B$ be joined by two curves $C_1$, $C_2$ and we imagine a current to flow from $A$ to $B$ along $C_1$ and then from $B$ to $A$ along $C_2$, we have a closed circuit and we know that the resultant of the magnetic intensities at $O$ due to $C_1$ and to $C_2$ vanishes. If we now reverse the direction of flow along $C_1$ we see that the current from $A$ to $B$ along two different paths produces the same effect at $O$. The effect at any point $O$ of a current flowing between two points $A$, $B$ is thus entirely independent of the path but depends only on the position of the two points. Now place $A$ at $O$, $B$ anywhere else, and for convenience choose the path $OB$ to be a straight line. By symmetry, the field due to $OB$ is directed along $OB$; let its magnitude be $\varphi(r)$, $(r = AB)$. To get the field due to an element of current $BB'$ we may replace it by a current flowing along the broken rectilinear path $BO$, $OB'$. We are thus led

to the resultant of two intensities, one pointing along $BO$ of magnitude $\varphi(BO)$, the other along $OB'$ of magnitude $\varphi(OB')$. In this we recognize the field of a doublet whose poles coincide with $B$, $B'$ and act radially with a force $\varphi(r)$.

This method, while much shorter, does not, however, cover the cases where the field becomes infinite near the element of vector.

The first of the examples cited is that of a doublet; the second becomes one, if we let the poles repel with a force equal to the distance.

Before going back to the Biot-Savart field and its generalization, we must point out one property of the fields due to doublets, namely, that the lines of force always lie in planes passing through the axis of the doublet. Pass the plane $\pi$ through a point $O$ and the doublet $AB$. The field at $O$ due to the pole at $A$ is directed along $OA$; the field due to the pole of opposite sign $B$ is similarly directed along $OB$. The field due to the doublet, being the resultant of these two vectors both of which lie in the plane $\pi$, also lies in $\pi$, as stated.

Now the field of Biot and Savart at any point $O$ is perpendicular to the plane $\pi$ containing the element of current and the point $O$. Generalizing it, by superposing a "null"-field, will therefore only complicate it, since the null-field always lies in $\pi$. It might also be pointed out that no modifications of the Biot-Savart law will ever make the force between an element of current and a magnetic pole obey Newton's third law, for the force on the pole will always have a component perpendicular to the line joining the two.

Whether the result established be of more than theoretical interest, I cannot say. If electricity did flow in open circuits, experiment would decide between the different possible laws. But Maxwell's displacement currents prevent that possibility by closing all circuits. Even the ideal element of current, a moving electron, is spoiled by the displacement currents as far as testing the theory is concerned.

The idea of null-fields could be extended to surfaces. We would be looking for laws of action of an element of surface that yield null results when the effect of a closed surface is computed. I have worked out such fields, along similar lines. The second method employed could probably be made to yield results for closed subspaces in spaces of higher number of dimensions than three.

CORNELL UNIVERSITY,
September 25, 1922.

## CORRECTIONS.

*Mobilities of electrons in hydrogen.* LEONARD B. LOEB, vol. 20, p. 397, November, 1922.—A blunder was made in reducing the equation for electron mobility in hydrogen as determined experimentally for a plate distance of 2.025 cm to an equation applicable to any plate distance $d$. The equation reduced to 760 mm pressure should be

$$K = 6.67 \times 10^5 \Big/ \left[ 97.2 + \frac{V_0}{d} \left( \frac{760}{p} \right)^{3/4} \right]$$

instead of that given at the top of page 402 of the paper.

*On the influence of surface tension on the efflux of a liquid in jet form.* JULIUS HARTMANN, vol. 20, p. 738, December, 1922.—On page 735, 1/50 should be 1.50. On page 738, in Figure 11, a-c, the second and third pictures should be interchanged. On page 743 in Figure 15, the values for air are given by circles, those for ether vapor by crosses, instead of as stated.

# PROCEEDINGS

OF THE

# AMERICAN PHYSICAL SOCIETY.

## MINUTES OF THE CAMBRIDGE MEETING, DECEMBER 27, 28 AND 29, 1922

THE 24th Annual Meeting (118th regular meeting) of the American Physical Society was held in Cambridge, Massachusetts, on Wednesday, Thursday and Friday, December 27, 28 and 29, 1922. The sessions on Wednesday and Friday were held in Room 4–270 of the Massachusetts Institute of Technology, and the sessions of Thursday were held in the lecture room of the Jefferson Physical Laboratory of Harvard University. The presiding officers were Theodore Lyman and C. E. Mendenhall, President and Vice-President of the Society respectively. On Thursday morning there was a joint session with the American Astronomical Society, and on Thursday afternoon the annual joint session with Section B was held, Professor F. A. Saunders, Chairman of Section B presiding. The attendance of members and friends varied from two hundred to two hundred and fifty. On the evening of Friday, December 29, there was a dinner of members of the Society and friends at the Harvard Union, attended by about two hundred persons. The arrangements made by the local committee for the entertainment of the members were most excellent, and the meeting was generally considered one of the most successful that the Society has held. There were numerous receptions, exhibitions and excursions arranged in connection with the general program of the American Association for the Advancement of Science, which were taken advantage of, as far as possible, by the members of the Society.

The program of the Physical Society consisted of sixty-six regular papers, three of which were read by title. Six papers from the program of the American Astronomical Society were presented at the joint session, and at the session with Section B there was an address by the retiring Vice-President entitled, "Certain Allurements in Physics." This was followed by a symposium on "Ionization Potentials and Atomic Radia-

tion," consisting of three addresses, as follows: "The Interpretation of Critical Potentials," by K. T. Compton, Princeton University, "Atomic Structure from Spectroscopic Consideration," by Paul D. Foote, Bureau of Standards, and "Ionization and Astrophysics," by Henry Norris Russell, Princeton University.

The regular Annual Business Meeting of the American Physical Society was held on Friday morning, December 29, 1922, at 11 o'clock. A canvass of the ballots for officers resulted in elections for the year 1923 as follows:

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| *For President:* | Charles E. Mendenhall |
| *For Vice-President:* | Dayton C. Miller |
| *For Secretary:* | Harold W. Webb |
| *For Treasurer:* | George B. Pegram |
| *For Members of the Council, Four-year Term:* | F. C. Brown<br>A. Ll. Hughes |
| *For Managing Editor of the Physical Review, Three-year term:* | G. S. Fulcher |
| *For Members of the Board of Editors of the Physical Review, Three-year term:* | A. H. Compton<br>E. H. Kennard<br>Leigh Page |

At the meeting of the Council held on December 29, 1922, three persons were elected to Fellowship; thirteen were transferred from Membership to Fellowship; and thirty were elected to Membership. *Elected to Fellowship:* Charles Galton Darwin, Mayo Dyer Hersey, Paul A. Heymans. *Transferred from Membership to Fellowship:* William T. Bovie, C. J. Davisson, C. O. Fairchild, R. L. Hartley, Thomas C. Hebb, Raymond Heising, Clarence Wilson Hewlett, G. E. M. Jauncey, Leonard B. Loeb, G. M. J. Mackay, F. W. Peek, Jr., R. B. Sosman, Leonard Thompson Troland. *Elected to Membership:* Mildred Allen, Alice H. Armstrong, Eric A. Arnold, Rollin Smith Baldwin, Russell S. Bartlett, W. G. Brown, Roy W. Chesnut, George L. Clark, E. R. Gray, Frederick H. Getman, Carleton D. Haigis, Grace Hazen, Otis P. Hendershot, C. N. Hickman, J. H. Hudson, Ittai Luke, Bradford Noyes, Jr., Harold F. Pierce, Hillel Poritsky, I. I. Rabi, Nils Riffolt, Charles Blacknall Robertson, H. Rossbacher, Richard G. Sagebeer, Frederick E. Sears, Thomas McNider Simpson, H. Grayson Smith, Roy C. Spencer, John W. Then, Albert L. Thuras.

The Secretary reported that during the year there had been 168 elections to Membership and that resignations of 39 had been received. Seven persons had died during the year. The total Membership at the

present time consists of 7 Honorary Members, 468 Fellows and 1045 Members, making a total of 1520.

The abstracts of all of the papers presented in the program of the Physical Society are given in the following pages.

DAYTON C. MILLER, *Secretary*.

## ABSTRACTS OF PAPERS.

1. **A theory for the Bumstead electroscope.** H. S. READ, Cornell University.—By equating the work of the electric field on the leaf to the increase in gravitational potential energy due to deflection, the following equation has been deduced for the small deflection $p$ of the gold leaf as a function of the leaf potential $E$, the two electrode potentials $+B$ and $-B$, the leaf length $l$, the distance $s$ of the leaf from either electrode, the capacity $c$ of the leaf with either electrode, the gravitational force $mg$ on the leaf, and a proportionality constant $k$.

$$p = k[cEBls/(mgs^2 - cEBl)].$$

Actual calibration curves for an electroscope were found to agree with the computed curves. The sensitivity $p/E$ depends on $s$, $B$, $l$, and $m$ and for working conditions is almost independent of $E$. It may be increased indefinitely by making $(mgs^2 - cEBl)$ approach zero. A sensitivity of 1,000 scale divisions per volt has been used. This simple electroscope recommends itself both because of its great sensitivity and because of the ease of adjustment over a wide range of sensitivity.

2. **The thermal emissivity of water.** MILDRED ALLEN,[1] Wellesley College.—The heat supplied to the water was measured by the electrical input in a coil. The vessel was mounted on the pan of a balance in order to take account of the evaporation. The heat radiated was taken up by a black cone cooled by circulating water. Beside the values of the emissivity obtained, results were given for the evaporation.

3. **The percentage bridge in the measurement of low electrical resistances.** A. C. LONGDEN, Knox College.—The percentage bridge as described in the Physical Review, Vol. 24, p. 349, 1907, has been modified in such a way as to make it a precision instrument for measuring low resistances. The success of the Kelvin double bridge depends largely upon its ability to carry very heavy currents. By arranging the percentage bridge so that it will carry equally heavy currents, it has been given even greater sensitivity than the Kelvin bridge. On account of its simplicity, it is a more convenient instrument to use and has fewer sources of error than the Kelvin bridge, and it yields results fully as accurate and with considerably less current.

4. **Note on some mechanical effects of a sliding electric contact.** K. S. VAN DYKE, Wesleyan University.—While fingering the output terminals of an audio-frequency vacuum tube oscillator several years ago, the author discovered that the note of the oscillator became audible as the finger slid over the binding post, and that the sliding finger experienced the sensation of vibrating. Investigation of the effect showed that if a conductor of small inertia is rubbed over a more massive conductor from which it is separated by a thin dielectric while an alternating e.m.f. is applied between the two conductors, variations in sliding friction occur such as would be expected from the alternating electrostatic attraction between the two. Torsional vibrations of a body have been maintained by this periodically varying sliding friction, and the vibration shown on a screen by means of a mirror carried by the vibrating body. As is to be expected the sound heard from the sliding body corresponds to the octave of the applied potential though the fundamental itself is heard if a biasing direct potential is applied with the alternating. With the dry finger, its skin serving as the dielectric,

[1] Introduced by A. G. Webster.

the effect is so sensitive that the double frequency of the oscillator is often heard when but one terminal of the oscillator is touched, the output circuit then being completed by leakage through the body and the floor. By stroking a bar longitudinally with a finger of one hand while the other hand touches the output terminal of the oscillator, various modes of vibration of the rod can be elicited at will by tuning the electric oscillator to the half frequency of the desired partial.

After the observations above presented were completed it developed that the effect is not a new one. Elisha Gray, in 1873 (W. H. Preece, The Telegraphic Journal, Sept. 1, 1877), noted this "*finger effect.*" In 1921 Johnsen and Rahbek demonstrated a loud speaking telephone before the Institution of Electrical Engineers in London in application of the same effect (The Engineer, June 3, 1921, p. 600). The present report is given to recall to scientific literature an effect long forgotten, and to point out that with vacuum tubes in common use demonstration of the effect becomes exceedingly simple, and its use as a *method of eliciting desired partials from vibrating bodies* quite convenient.

**5. The effect of an intermittent direct current under varying conditions on the e.m.f. associated with a metal plate in a solution.** R. D. KLEEMAN and W. F. WINTER, Union College.—Three metal plates *a, b, c* of the same material were partly immersed in a solution of a salt of the metal, an intermittent direct current of about nine pulses per second was sent from *a* to *b* through the solution, or vice versa, and the e.m.f. between the plates *a* and *c* was measured by means of a galvanometer during the periods that the intermittent current was not acting. Deflections were observed while the intermittent current was gradually increased to .016 amp/cm$^2$ and then gradually decreased. Various curves were obtained, depending on the metal and the solution and on the direction of the current, the deflection sometimes increasing steadily, sometimes passing through a maximum and then decreasing, sometimes passing through a maximum and then through a minimum. Moreover, the curves obtained on decreasing the exciting current are not the reverse of those obtained with increasing current. These complicated results may be explained by assuming an ionic segregation polarization near the plates in the layer of segregated ions which previously has been suggested (Kleeman, Phys. Rev. 20, 174, 1922) as the cause of the voltaic e.m.f. This polarization is largely of the nature of a reflex action which may be sudden and violent and which possesses properties of inertia and fatigue.

**6. Variation of the velocity of sound in sea water with temperature.** E. B. STEPHENSON, Engineer Section, War Department.—The velocity has been measured at different temperatures from 0° to 20° C, and the average increase found to be 2.8 meters per degree C. This value includes effects due to changes in density and salinity which are small compared with the temperature effect. The method used is described in detail in an article in the Physical Review 21, 181, 1923. The average velocity over distances of 10,000 to 15,000 meters was determined by measuring the time required for the sound to travel these known distances through sea water of known temperature. Numerous additional temperature studies by means of deep sea thermometers at different depths and different places in Block Island Sound have given the variations of the temperature with the seasons and with the depth. The velocity of sound and temperature studies show the waters in this area to be homogeneous for sound transmission over long distances. The experimental work was done by the Subaqueous Sound Ranging Section of the Coast Artillery Corps at Fort Wright, N. Y.

**7. A new feature in the production of uniform speeds of rotation.** F. WENNER, Bureau of Standards.—A direct current motor is operated with a loose flywheel which is driven from the motor by means of a spring which exerts a torque in excess of the retarding torque caused by air friction, but is limited in this action by a stop. The

arrangement is such that the spring can not divide its force between the loose flywheel and the stop. Consequently it exerts a driving torque for only such portions (approximately half) of the time as may be necessary to supply the power lost by air friction, unless the motor is accelerating. As the retarding and driving torques are both small, and the inertia of the flywheel is large, the acceleration of the flywheel must in any case be small. When the spring comes against the stop it closes an electrical connection in an auxiliary circuit and thus causes a definite increase in the power supplied to the motor. In operation this contact is closed whatever fraction of the time is necessary to supply the extra power required to keep the motor definitely synchronized with the flywheel. Means are provided for limiting the hunting or oscillation in phase between the motor and the loose flywheel. One element of this means in effect counteracts completely the time lag in the change in power supplied to the motor following the opening or closing of the contact in the auxiliary circuit. Within limits the frequency and amplitude of the oscillation can be made as desired. For the assembly with which we are working a particular adjustment makes the frequency about ten cycles per second and the amplitude probably less than one degree. In so far as changes in speed are concerned the device behaves somewhat the same as if a flywheel having a very large moment of inertia were keyed to the shaft of the motor.

**8. The effect of longitudinal moment of inertia upon dynamic stability of airplanes.** EDWIN B. WILSON, Harvard University.—A discussion of the decrease of the damping and the increase of the period of longitudinal and lateral motion of the airplane when the moment of inertia is increased by the transfer of mass along the longitudinal axis without the displacement of the center of gravity. It appears that relatively speaking the lateral motion is more largely affected than the longitudinal motion, but that the effect of any practicable change in the distribution of matter in a given reasonably stable machine is likely to be less than can readily be determined experimentally in full flight tests.

**9. A thermoelectric effect.** A. S. EVE, McGill University.—If a portion of a uniform homogeneous wire is subjected to strain (torsion or tension), if it is altered by heating or cooling, and if a junction between the changed and unchanged portions is heated or cooled, then a thermoelectric current will generally result. This was established by Becquerel (1829), Le Roux (1867), Kelvin, and others. In particular, Trouton (Proc. Roy. Dublin Soc., p. 171, 1886) investigated the *effect of moving a flame along a wire* connected to a sensitive galvanometer. Comparatively large effects may be found for iron and nickel, the current produced being in the direction of the moving flame. In some other substances the current is in the reverse direction. The present communication deals with the effect of moving a pad dipped into liquid air along a homogeneous wire. The current in iron is now reverse in direction to that of the movement of the cooling agent. In some substances such as copper and platinum, the effect is very small. Both heating and cooling effects are specially well marked in the case of nichrome. Discontinuities in a wire may mask the effect. According to Benedicks the effect may be attributed to asymmetrical heating causing an electric current.

**10. On the physical composition of the earth's magnetic field in 1922.** LOUIS A. BAUER, Department of Terrestrial Magnetism, Carnegie Institution.—Chiefly on the basis of its own accumulated data, the Department of Terrestrial Magnetism has been enabled to make a new analysis of the earth's magnetic field and the fact has been confirmed that the magnetic forces observed on the earth's surface arise to the extent of about 93 per cent from magnetic or electric systems inside the earth. A somewhat larger portion than found by previous investigators, nearly 3 per cent, arises apparently from electric systems in the atmosphere, and the remaining portion, about 4 per cent, is apparently to be ascribed either to vertical electric currents which pass

through the atmosphere into the earth and out again, or to an effect similar to the deviation of the compass needle caused by forces set in operation during the earth's rotation, or to both causes combined. In line with the author's previous results, it is found that the intensity of magnetization is greater in the equatorial regions than in latitudes north or south; for example, on the average, the intensity of magnetization is about 17 per cent greater at the equator than for the parallels of latitude 60° north or south. It is also again found that the earth's magnetic moment is diminishing; the annual rate of decrease during the past 60 years has been about one part in 1,200. The period for which reliable observational data are available is not yet of sufficient length, however, to say whether this rate of decrease will continue or whether, after a lapse of years, a turning point will be reached after which the earth's magnetic moment will begin to recover a previous value. The possible physical causes for some of the facts obtained from the analysis were briefly discussed.

**11. Effect of frequency on permeability.** LEIGH PAGE, Yale University.—The object of this paper is to deduce a relation between the permeability of paramagnetic substances in weak fields and the frequency of the impressed field. A group of molecular magnets which have just suffered a collision will have a statistical distribution in direction of their magnetic axes, determined by the magnitude of the field at the time of collision. During the interval of time elapsing before the next collision, the axes of this group will be displaced by the alternating field. Summing up over all such groups, an expression for the permeability is found. In the case of a solid, where a strong molecular field is present, the permeability remains practically constant at low frequencies, then rises to a maximum, decreases to a value below one and finally rises gradually to the limiting value unity at very high frequencies. In the case of a gas, where the molecular field is negligible, the permeability decreases continually with increasing frequency to a minimum a little less than one, and then rises to the limiting value unity at very high frequencies. Details will be contained in a paper to be published in the Physical Review.

**12. The power loss in condensers with liquid dielectrics.** LOUISE S. MCDOWELL, Wellesley College.—The capacity and equivalent series resistance of condensers with the liquid dielectrics—castor oil, olive oil, oil of turpentine, paraffine oil, toluene, xylene, benzene—were measured for frequencies ranging from 600 to 3,600, and in some instances to 1,500,000. For the lower range a capacity-bridge method was employed, using a special form of bridge developed in the Cruft Laboratory. For the range from 33,000 to 1,500,000 an ordinary resonance method was used. As the capacity remained practically constant, the cause of the loss was sought in the variation of the equivalent series resistance with frequency, and was found to be due chiefly to leakage since, with the exception of castor oil, the values of the resistance fitted approximately the equation $R_s = 4d\lambda T^2/A\epsilon^2$, obtained from the general expression for the impedance of a leaky condenser when the specific conductivity, $\lambda$, is small. At low frequencies, however, the observed values were too great. This additional resistance was not the result of added impurities or change in temperature, and did not accord with the equation of von Schweidler for loss due to dielectric absorption. For castor oil, the values of the series resistance fitted fairly well the equation $R_s/T^2 = a_1/\epsilon_1^2 + a_2/(\beta_2 T^2 + \epsilon_2^2)$, which would indicate two capacities in series.

**13. Piezo-electrically driven tuning forks and rods.** W. G. CADY, Wesleyan University.—In previous papers (Phys. Rev. 17, p. 531, 1921, and 19, p. 381, 1922; Proc. Inst. Radio Eng. 10, p. 83, 1922) the piezo-electric resonator and its application in the production and stabilization of high frequency currents have been described. It has now been found possible, with the aid of Rochelle salt crystals and thermionic amplifiers, to drive a tuning fork, or to keep a long steel rod in longitudinal vibration, and thus to obtain a sustained musical note. In the case of the tuning fork, two methods

are available. If the fork is of high pitch with rather wide spacing between prongs, a long plate cut from a Rochelle salt crystal may be cemented lengthwise between its base and a massive block of metal. The plate is provided with two pairs of tinfoil coatings. If the latter are connected to the input and output of the amplifier, the fork will vibrate at its natural frequency, producing periodic stresses in the crystal plate and thus, through the piezo-electric action, impressing periodic potential changes on the input grid. In the second method, the fork is mounted in the usual way but has a Rochelle salt plate cemented endwise to each of its prongs near the tip. Each plate has a pair of tinfoil coatings, and the connections are the same as in the first method, the only difference being that the inertia of the plates themselves now furnishes the necessary reaction. A long, flat steel rod may likewise be kept in vibration by means of four Rochelle salt plates, two being cemented on each side of the rod near its center. The plates have the usual tinfoil coatings and are connected in pairs, with due regard to polarity, to the input and output of the amplifier. This method is most convenient when notes of very high pitch are desired. It has not yet been found possible, however, to drive the larger sizes of tuning forks by means of piezo-electric crystals.

**14. The Joule-Thomson effect in carbon dioxide.** E. S. BURNETT, University of Wisconsin.—Experimental observations on the variations of temperature and pressure experienced by $CO_2$ vapor and liquid when subjected to expansion through radial flow porous plug apparatus of the type described by Burnett and Roebuck (Phys. Rev. 30, p. 529, 1910) in 1910 have been obtained over a pressure range of approximately 50 atmospheres, extending roughly from 20 or 25 atmospheres to 70 or 75 atmospheres, at temperatures varying from 120° C to — 20° C, thus including the saturation field and the critical point region. These results agree well with observations reported by Jenkin and Pye (Phil. Trans. Royal Soc. A. 213, p. 107, 1914; 215, p. 380, 1915) on throttling experiments with $CO_2$ vapor and liquid, covering somewhat lower pressure and temperature ranges than those of this work, but overlapping. These combined data have been grouped into "isenthalpic" throttling curves on a pressure temperature chart. An empirical algebraic formulation has been evolved which represents these curves within the limits of the experimental uncertainty of the observations, and enables us to compute, within those limits, the Joule-Thomson effect for $CO_2$, and also various thermal relations associated therewith, as continuous functions of temperature and pressure over a pressure range from zero to 100 atmospheres and at temperatures from 120° C in the superheated vapor field down through the liquid phase to the solid phase boundary which extends from — 56° C at the triple point to — 54° C at 100 atmospheres.

**15. Note on the quantum theory of the helium arc spectrum.** J. H. VAN VLECK, Harvard University.—While the quantum theory has furnished a remarkable explanation of the "spark" spectrum emitted by ionized helium, it has not yet been successfully applied to the "arc" spectrum radiated by neutral helium atoms. In two articles Landé has endeavored to evaluate theoretically the frequencies of the helium arc spectrum (Phys. Zeit. 20, p. 228, 1919; 21, p. 114, 1920). In the first article certain terms involving the perturbations were neglected, and only a portion of them were included in the second paper. A simple computation shows that if all, rather than part, of these neglected terms are inserted, they cancel out entirely. Hence, the calculations in the second article are inaccurate, while those in the first article are correct if the quantum conditions used are valid. These conditions, however, appear unsatisfactory to the writer, and if the generally accepted Schwarzschild quantization based on angle variables be substituted, the series "term" $(n, n')$ of the orthohelium spectrum corresponding to the stationary state $(n, n')$ is $N(n+n')^{-2}[1+n(n+n')^{-1}(9/8n^3 - 1/8n^4) + \ldots]$ where $n$ and $n'$ are integers. When this formula is used, the disagreement with experiment proves to be considerably greater than in either of Landé's

original theories, and this suggests that existing quantum conditions cannot be applied without some modification to atoms with more than one electron. Epstein reaches a similar conclusion because of the difficulties confronting his quantum theory of the helium arc spectrum (Die Naturwissenschaften, p. 230, 1918).

**16. On the explosion spectra of the alkaline earth metals.** R. A. SAWYER and A. L. BECKER, University of Michigan.—In 1920, J. A. Anderson (Astrophys. J. 51, 37, 1920) obtained exceedingly high temperature spectra by discharging a large condenser, charged to a high voltage, through a fine metal wire. In the course of some investigations on this light source the authors (Science, 54, 305, 1921) have replaced the metal wire by an asbestos fibre saturated with an aqueous solution of a salt of any chosen metal. This modification of the original method has the advantage that any metal which occurs in soluble salts may thus be studied. The fibre is uninjured by the explosion and may be used repeatedly. The condensers used in this investigation were oil-immersed glass condensers with a total capacity of about 0.3 microfarad. They were charged to about 40,000 volts through a water rheostat from a one-kilowatt transformer, with current rectified by a kenotron. A heavy knife switch, closed under oil by a spring, discharged the capacity through the fibre. The explosion spectra of the chlorides of Ba, Ca, Mg, and Sr were photographed in the region $\lambda$ 2280–$\lambda$ 4550, in the first order of a 6-foot grating. After impurity lines are eliminated, the spectra are found to be almost pure spark spectra, chiefly made up of the doublets of the first and second subordinate series, $2p - md$, and $2p - ms$. The only arc line to appear is the fundamental singlet line $1S - 2P$. Its intensity with reference to spark lines is only about 1/10 as much as in the ordinary spark spectrum and approximately the same as in the spectra of the solar chromosphere and the class B stars. The first member of the Bergmann series of magnesium, $\lambda$ 4481, appears; also the barium line $\lambda$ 4350 whose series relation is unknown. No lines of Cl, H, or O were identified. In the spectrum of each of the metals used appear many of the lines of the other metals of the group, showing how small an amount of material is needed to give an explosion spectrum. These results are shown to agree with the temperature radiation theory of Saha (Proc. Roy Soc. A. 99, 135, 1921).

**17. On the resistance experienced by spheres moving through gases.** PAUL S. EPSTEIN, California Institute of Technology.—The results obtained by several authors for the resistance of spheres, small compared with the mean free path of the gas molecules, show a discrepancy. The first part of this investigation has therefore the object of checking their results and gives a complete agreement with the values found by Lenard. The second part contains the treatment of the resistance of large spheres on a kinetic basis.

**18. The physical significance of the constants involved in the complete law of motion of a sphere moving through a gas.** R. A. MILLIKAN, California Institute of Technology.—The constant $A$ in the complete law of fall $v = 6\pi\eta a v[1 + (l/a)(A + Be^{-c(a/l)})]$, when multiplied by mean free path $l$, is a measure of "slip," and is found by a combination of hydrodynamical theory with kinetic theory to have a lower limiting value of .7004. Its measured value is generally higher than this—a fact which denotes unambiguously specular reflection. The constant $(A + B)$ makes it possible to differentiate between "absorption and re-evaporation" and "diffuse reflection" and its experimental value indicates the latter, slightly modified by some mechanical roughnesses and a small percentage of specular reflection.

**19. Scattering of light by liquids.** FRANK B. KENRICK and W. H. MARTIN, University of Toronto.—A method of removing dust from liquids and of making visual measurements of the light scattered by pure dust-free liquids and liquid solutions is reviewed, and a photographic method of measuring the depolarization factor for the light scattered by liquids is described and some measurements are given of the value

of this factor for several of the mercury lines. The change of the depolarization factor with change of temperature is under investigation.

**20. The compressibility of metals at high pressures.** P. W. BRIDGMAN, Harvard University.—A new method has been developed for the measurement of the linear compressibility of solids accurate enough to give changes of compressibility with pressure and temperature. The method has been applied to some thirty metals at two temperatures, 30° and 75°, and to a maximum pressure of 12,000 kg/cm². In general the variation of compressibility with pressure, or the variation of thermal expansion with pressure, is of the order of magnitude of 10 times the change of volume under the same pressure, but the factor may vary in individual cases from 3 to 30. In the case of some metals not crystallizing in the cubic system, it has been possible to establish the fact that the linear compressibility may vary in different directions by a factor of several fold. It is possible to calculate from the data that the specific heat of a metal decreases at high pressures by a factor several times the proportional decrease of volume.

**21. The effect of pressure upon optical absorption.** FRANCES G. WICK, Vassar College.—A study of the effect of pressure upon the absorption of light in a few solutions and solids was made at the suggestion of P. W. Bridgman and the experiments were performed in his laboratory with pressure apparatus designed by him. The specimen was mounted in an observation chamber with glass windows and pressure was applied by a hand pump of 1,000 kg/cm² capacity, connected with an intensifier of piston ratio 4 : 1. Light from a carbon arc made parallel by a lens was transmitted through the specimen to the collimator of a spectrograph and photographs of the absorption spectra were made at normal pressure and at high pressures up to 3,500 atmospheres. The absorption spectra of neodymium salts are rich in bands of unusual sharpness and the effect of pressure upon aqueous solutions of these salts was more pronounced than upon those of praseodymium and erbium. Dilute solutions of neodymium nitrate and neodymium ammonium nitrate showed the following effects due to increase of pressure: (1) An unsymmetrical narrowing and an intensifying of some of the absorption bands but not of others, the narrowing taking place principally on the red side; (2) a slight shift in the position of some of the narrowed bands, usually toward the violet but in one case toward the red; (3) the bringing out, at high pressure, of bands less prominent at normal pressure. Solutions of cobalt chloride, the synthetic ruby, and certain of the samples of colored glass showed an effect with increase in pressure which was in the same direction as that known to be due to a lowering of temperature. The results obtained indicate that in the case of both solutions and solids, an increase in pressure is similar in effect to a lowering of temperature in some respects but not in all. In the case of solutions, the effect of increasing pressure is similar to that of decreasing the concentration but these effects are also different in some respects. The effects are small and the results obtained are principally qualitative.

**22. The photo-electromotive effect in selenium.** E. H. KENNARD and C. MOON, Cornell University.—This is a report of some preliminary results of an investigation of the change in the contact potential of selenium by light. Measuring the contact potential by the well-known ionization method (Phys. Rev. 9, p. 58, 1917) and illuminating with one line at a time of the spectrum from a quartz mercury lamp, which had been calibrated with a thermopile for other work by Dr. Moon, the authors found little variation in sensitiveness with wave-length, the effect being perhaps 20 per cent greater in the violet and 10 per cent greater in the yellow and green than for the same energy in the ultraviolet. With light from a 100-watt gas-filled tungsten lamp one foot away filtered through a water-cell and a Wratten-Wainwright green filter No. 62 and measured by a thermopile, the change in contact potential was approxi-

mately proportional to the cube root of the intensity over a range of intensity of at least 1 to 200. The change in resistance, measured practically simultaneously, was nearly proportional to the change in contact potential for intensities from 10 to 200 but fell off much more rapidly at lower intensities; the same thing was true in another run taken without water-cell or filter.

**23. Quantum theory of photographic exposure; third paper.** LUDWIK SILBERSTEIN, Eastman Research Laboratory.—The purpose of this paper is, first, to take account of the absolute energy values of the exposures used in the photomicrographic experiments described in the first two papers (Phys. Rev. **19**, 443, 1922, and Phil. Mag., July and Nov., 1922) on the subject, which values have since been measured, and, in the second place, to deduce from the fundamental formula given before the integral or "density" formula for a certain type of emulsions (viz., having an exponential frequency curve of grains) and to compare it with the experimental results obtained with x-rays by R. B. Wilsey at the Eastman Laboratory. The formula, which is $D=2 \log (1+\alpha E)$, contains but one parameter $\alpha$. This being appropriately chosen, the whole set of 14 observations, ranging over exposures $E$ from 1 to 64 $\sqrt{2}$, is covered by the formula within the experimental error limits. The treatment of the first point, which shows that only a small fraction, about $10^{-5}$ to $10^{-4}$, of the area of a silver halide grain is sensitive to light, affords an opportunity for amplifying the originally proposed theory for grains whose sensitivity is confined to "spots" distributed haphazardly, the fundamental assumption of the discrete structure of light being retained without change. Formulæ are developed for the experimental determination of the size of the spots and of their average number per grain.

**24. Tracks of alpha rays in gases.** R. W. RYAN and W. D. HARKINS, University of Chicago.—Using an apparatus of the Shimizu-Wilson type in connection with a Universal moving picture camera and a Cooke F2 lens, the writers have obtained a set of about ten thousand photographs showing approximately forty thousand tracks of alpha particles in air. The photographs give no indication of a disintegration of any of the atoms of air. The source of alpha particles used thus far is polonium, but a more powerful source will be tried later, the difficulty of the latter being the exclusion of $\gamma$-rays. A number of the tracks show collisions between the alpha particle and an atom of one of the gases in the air (usually nitrogen). For example, one track shows an alpha particle which is turned through an angle of 125° and then rebounds a distance of 0.5 cm, while the nucleus which is hit moves forward 0.35 cm, leaving a bright track, the direction of which bisects the angle between the two limbs of the alpha ray track. This indicates that the effects are purely mechanical. The extremely rare occurrence of such sharp bends in the alpha ray tracks proves, as in Rutherford's scintillation experiments, that the nucleus of the nitrogen atom is extremely minute. Another type of split track has also been observed. In this the initial alpha ray track is continued as a straight line to its end, but from some point on it a side track branches off. The origin of such a type of forked track is uncertain, since it does not seem to be in accord with the ordinary laws of impact, though the discrepancy may be apparent and not real. One similar track was obtained in hydrogen by Bose (1917), so it may be that the form of the track is due to the lightness of the atom which is hit. The investigation is being continued with heavy gases.

**25. Band lines in the secondary spectrum of hydrogen.** GORDON S. FULCHER, Corning Glass Works.—With the help of recent measurements by Merton and Barratt (Trans. Roy. Soc., p. 388, 1922), additional band lines have been discovered. Each group is found to consist of five lines instead of three, and these are regularly spaced, the wave-length intervals being successively 2, 3, 4, and 5 times 2.70 A (red bands) and 2.98 A (green bands). The red groups are as follows, intensities being given in brackets:

1. 6018.29(10) ; 6023.74(7) ; 6031.80(10) ; 6042.70(5) ; 6056.10 (5)
2. 6121.76(10) ; 6127.40(9) ; 6135.34(8) ; 6146.17(3) ; 6159.58 (4)
3. 6224.81(9) ; 6230.23(7) ; 6238.39(8) ; 6249.15(3) ; 6262.49 (4)
4. 6327.07(8) ; 6332.46(5) ; 6340.57(6) ; 6351.28(1) ; 6364.64 (2)
5. 6428.10(5) ; 6433.47(2) ; 6441.50(3) ; 6452.13(0) ; (6465.22)(0)
6. 6527.35(4) ; 6532.62(1) ; 6540.53(2) ;

The similar groups in the green and yellow are:

1. 5303.15 (8) ; 5309.03(4) ; 5317.90 (5) ; 5329.74 (1) ; 5344.82(1)
2. 5419.90 (6) ; 5425.96(3) ; 5434.83 (5) ; 5446.70 (0) ; 5461.50(1)
3. 5537.45 (7) ; 5543.41(2) ; 5552.52 (4) ; (5564.53)(2) ; 5579.47(0)
4. 5655.75 (5) ; 5661.72(3) ; 5670.89 (3) ; (5683.05)(2) ;
5. (5774.98)(7) ; 5789.85 (1) ;
6. (5895.93)(3) ; (5910.15)(2) ;
7. (6018.29)(10) ; (6031.80)(10) ;

The doubtful lines are enclosed in brackets. λ 6127.40 is probably double, the band line being λ 6127.20(7). An interesting feature of these lines is that the wave-length differences are more constant than the frequency differences. All these lines are low-voltage lines, relatively weak in the condensed discharge, and those that have been tested show no Zeeman effect.

**26. The dispersion of the optical constants of mercury.** BRIAN O'BRIEN and L. P. WHEELER, Yale University.—All the observations were made with a vertical Jamin circle fitted with quartz lenses, Foucault-Glan polarizer and analyzer, and Babinet-Soleil compensator. The separate lines of the mercury arc spectrum were thrown on the slit of the Jamin circle by a monochromatic illuminator of the Littrow type. For the visible range the prism train of the illuminator consisted of two quartz prisms with a mercury amalgam reflector on the back face of the second, while for the ultraviolet lines a single prism with a plate of polished silicon as reflector was used. The field was observed in the customary manner for the visible lines, while for the ultraviolet lines a fluorescent screen of potassium uranyl sulphate placed with its normal at an angle of 30° to the telescope axis was viewed by a short focus ocular from the side. With this arrangement measurements could be made with the desired accuracy down to the wave-length 3022 A. For some of the lines observations were taken by both methods and showed very satisfactory agreement. The reflecting surface was prepared for each set of readings in the manner previously described (Wheeler, Phil. Mag. **22**, p. 229, 1911; also Am. Jour. Sci. **32**, p. 85) and is known to give a surface entirely free from contamination. It is believed that an accuracy of one half per cent has been attained throughout the entire range, λ 5770 to λ 3022 A. Aside from having obtained what we believe to be the first thoroughly reliable data for optical constants specific of a material as distinguished from those affected by surface conditions, the most important result of this work is the appearance of a minimum in the curve for the index of refraction at about λ 3100 A. Although the curve for the absorption coefficient does not show a similar minimum within the observational range, there is evidence from its changing curvature, coupled with the fact that this minimum comes at a somewhat shorter wave-length than that for the index of refraction in the case of several other metal surfaces, that such a minimum exists for mercury not far beyond the region to which it was feasible to extend the measurements.

**27. The infra-red band spectrum of methane.** J. P. COOLEY, University of Michigan.—Previous investigations on methane have shown three absorption regions which Coblentz places at 7.7 μ, 3.31 μ, and 2.35 μ. By using the higher dispersion of a grating spectrometer all of these have been partially resolved into lines. About fifty lines in the 3.31 μ region have been measured and fitted into two parabolic series, one on each side of the center of the band. Between these and masking the first line of the

positive or longer wave-length series, lies a narrow region of intense absorption corresponding to the "zero branch." Here the lines are too closely packed to be resolved but the composite structure is indicated by a large shift of the maximum absorption when the thickness of the layer of gas is changed. The band at 7.7 $\mu$ is similar in structure. Twelve lines in the positive series and eighteen in the negative series have been measured but again in the zero branch no fine structure appears

According to the quantum theory the frequency difference between adjacent lines is given by $\Delta V = h/4\pi^2 I$. By this equation the *moment of inertia of the molecule* in the first rotational state represented in the region at 3.31 $\mu$ is given as $5.6 \times 10^{-40}$ gm cm$^2$, and in the region at 7.7 $\mu$ as $9.0 \times 10^{-40}$ gm cm$^2$.

**28. The temperature of a black sphere which is exposed to radiation from one direction.** ARTHUR TABER JONES, Smith College.—A theoretical study has been made to determine whether the common assumption that the *temperatures of meteorites* just before they enter the atmosphere of the earth are close to the absolute zero, is correct. It is assumed that the distribution of temperature in the sphere is a steady one, and that the temperature of the surface may with sufficient accuracy be represented by a finite power series of cosines of angular position around the sphere. The coefficients in this series are determined by making the temperature given by the series agree at chosen positions on the sphere with the temperature given by a more accurate but less tractable expression. For a sphere 10 cm in diameter, having a thermal conductivity of 0.003 cal./cm sec. deg., and exposed to solar radiation of intensity equal to that which reaches the earth, it is found that the difference between the temperature at the point of the sphere nearest to the sun and the temperature at the point farthest from the sun is about 45°, and that the temperature at the center of the sphere is close to 0° C, which is much higher than the temperature of a meteorite had been supposed to be.

**29. Velocity of sound in free air and type of air structure.** ALEXANDER MCADIE, Blue Hill Observatory.—The War developed sound ranging and much good work was done in locating guns. Given three reporting stations with known distances from a central point in the rear, good chronoscopes and quick photographic processes, it was possible to locate the source of sound quite closely. The present problem is different. Distances from the source of sound are definitely known and the purpose is to correlate variation in speed over distances ranging from 2,500 to 3,700 meters and time intervals varying from 9 to 11.5 seconds, with changing conditions of wind, temperature, humidity, and turbulence; also with the type of air structure. Several thousand observations are available. The speed is always greater than customary formulæ indicate, allowing for wind directions and velocities. The value 331.74 meters per second for dry air at freezing temperature and at sea-level pressure is used, but this value appears to be questionable for free air work.

**30. A quantum theory of optical dispersion.** CHARLES G. DARWIN, California Institute of Technology.—The Bohr theory gives a dispersion formula depending on the frequencies of the electrons in their orbits instead of the absorption frequencies, and this is wrong. The present theory modifies the rules for the emission of light by electrons in such a way as to lead naturally to the correct formula. It shows promise of further extensions of the quantum theory in other directions.

**31. The complex anisotropic molecule in relation to the theory of dispersion and scattering of light in gases and liquids.** L. V. KING, McGill University.—It is well known that light scattered by various gases at right angles to the incident beam is not completely polarized. This is accounted for by Cabannes by assuming a simple anisotropic molecule containing a single dispersion electron acted on by unequal quasi-elastic forces in the three principal directions and hence capable of vibrating with three principal frequencies. The theory has now been extended to isotropic media

composed of complex anisotropic molecules containing any number of dispersion electrons whose principal directions are not parallel. All molecular orientations are assumed equally probable. In gaseous media, the intensity $I_s(\theta)$, scattered in a direction $\theta$ with the incident beam to a distance $r$ from volume $V$, comes out: $r^2I_s(\theta)/VI = \frac{1}{2}(\pi^2/\lambda^4)[(\mu^2-1)^2/n][6(1+\rho)/(6-7\rho)][1+(1-\rho)\cos^2\theta/(1+\rho)]$, where $I$ is the intensity of the unpolarized incident light, $\rho$ is the depolarization factor, $\lambda$ is the wave-length, and $\mu$ the refractive index corresponding to molecular density $n$. The corresponding formula for coefficient of extinction by scattering is $\kappa = (8\pi^3/3\lambda^4) \times [(\mu^2-1)^2/n](6+3\rho)/(6-7\rho)$. A remarkable feature of these formulæ is their invariance with respect to various details of molecular structure.

The scattering of light by dust-free liquids has been explained by Smoluchowski and Einstein as due to fluctuations of density arising from thermal agitation. It may be shown that equally probable orientations of complex anisotropic molecules within a volume of the dimensions of light wave would result in the scattered light being completely polarized, contrary to observation. It is concluded, therefore, that liquids have an extremely fine-grained crystalline structure, which is continually breaking up and reforming. Assuming energy of one degree of freedom to be associated with the random pulsations of these crystalline aggregates, we get: $r^2I_s(\theta)/VI = (\pi^2/2\lambda^4) \times (\mu^2-1)^2[6(1+\rho)/(6-7\rho)](RT\alpha/N)[1+(1-\rho)\cos^2\theta/(1+\rho)]$, where $R$ is the gas constant per gram molecule, $N$ is Avogadro's constant, $T$ is absolute temperature, and $\alpha$ is the adiabation compressibility. Martin has shown that the $I_s(\theta)$ varies as $1/\lambda^4$ for benzine and water, and for $\lambda$ 4358 A and 20° C obtained for $r^2I_s(\pi/2)/VI$ the values $26.0 \times 10^{-6}$ and $1.77 \times 10^{-6}$ for benzine and water, whereas the corresponding calculated values are $21.5 \times 10^{-6}$ and $1.85 \times 10^{-6}$. The formula also accounts for the observed relative scattering of some 20 organic liquids studied by Martin. This satisfactory agreement tends to justify the hypothesis of a crystalline structure for liquids which is also supported by observations of Debye, Keesom, and, more recently, of Hewlett on the scattering of x-rays by liquids.

**32. Short electric waves from the Hertzian doublet and the quartz mercury arc.** E. F. NICHOLS and J. D. TEAR, Nela Research Laboratories.—By an extension of methods previously described, the writers have obtained electric waves less than one millimeter in length. They have also successfully used two types of electric-wave receivers for measurements on Ruben's and Von Baeyer's longest heat waves from the quartz mercury arc, which they have obtained without using the quartz lens isolation method previously thought necessary. This radiation has been found to be partially polarized, with the electric vector in the direction of the axis of the arc.

**33. Experimental results in interior ballistics.** ARTHUR G. WEBSTER, Clark University.—The experiments are made with a gauge capable of directly measuring the variation of pressure in a gun by a continuous record, made by photography, the absence of oscillations in the gauge being obtained by using a straight spring of very great stiffness. In the bomb the curve is absolutely smooth, while in the gun the slight oscillations due to wave-motion are shown. The theory of the combustion of the powder is given and verified by experiment. A large number of curves is shown showing the relations of the various quantities involved. The results are compared with results obtained later at the U. S. A. proving ground at Aberdeen by entirely different instruments. It is believed that these are the first published experimental results obtained with a continuous gauge.

**34. The crystal structure of metallic selenium and tellurium.** MABEL K. SLATTERY,[1] Vassar College.—X-ray photographs were obtained by the powder method described by Hull and by Debeye and Sherrer. Both elements have been found to crystallize in a simple triangular lattice with *three* atoms associated with each point

[1] Introduced by Edna Carter.

of the lattice. For selenium, the side of the basal triangle $a$ is 4.34 A, while the axial ratio $c$ is 1.14. For tellurium $a$ is 4.44 A and $c$ is 1.33.

**35. Evidence from crystal structures in regard to atomic structures.** MAURICE L. HUGGINS, Harvard University.—If the extension of the Lewis theory of atomic structure proposed by the writer (Science, **55**, 459, 1922; J. Phys. Chem. **26**, 601, 1922) is correct, the valence electrons around an atomic kernel should tend to be in pairs opposite some or all of the faces of the polyhedron formed by the electron pairs or triplets in the outermost kernel shell (except for elements in the first row of the periodic table), this tendency being very weak for the most electropositive elements, and very strong for the most electronegative elements. As a result of this tendency it should be possible to predict the general arrangement of electrons and atomic kernels around each atom in many crystals; and often, especially if the crystallographic symmetry and axial ratios are known, the complete structure should be obtainable in this way for comparison with experimental results. In most of the metals, where all the atoms are electropositive in character, and in such crystals as the alkali halides and the alkaline earth oxides, sulfides, selenides, and tellurides, in which half of the atoms are electropositive, the atomic arrangements found by means of x-rays are such that the valence electrons cannot be opposite the faces of all the kernel shells. This was predicted from the theory, but cannot be considered as very good evidence, either for or against it, as other symmetrical kernel structures might fit the known crystal structures just as well. Excepting such crystals, however, the atomic arrangements which have been obtained are in strict accord with the predictions. In fact, there is not a single case, in which the relative positions of the atomic centers have been definitely determined, where these positions do not accord with the theory.

**36. On the abnormal reflection of x-rays by crystals.** WILLIAM DUANE and GEORGE L. CLARK, Harvard University.—The object of this paper is to report further researches on the abnormal reflection of x-rays by crystals (Proc. Nat. Acad., May, 1922; Phys. Rev., July, 1922). We have observed the phenomenon in four different crystals of potassium iodide. In the experiments we use x-rays in the continuous spectrum, having a great variety of wave-lengths. The x-rays reflected by the principal planes of the potassium iodide crystals obey the ordinary laws of reflection, but the abnormal reflection from the potassium iodide (what we have called the x-peak in the previous paper) does not obey the ordinary laws of reflection. If we turn the crystal through a given angle this abnormally reflected beam does not turn through twice that angle. Further, the wave-length of the reflected beam does not obey the equation $n\lambda = 2d \sin \theta$; in fact, it always has the same wave-length, and this wave-length is a good mean value of the wave-lengths of the lines in the characteristic x-ray spectrum of iodine.

With the ionization chamber of the spectrometer in a given position there are a number of positions of the crystal which reflect the x-peak into the ionization chamber. These positions of the crystal make equal angles with the positions it must occupy when its principal planes reflect x-rays into the ionization chamber; but these angles vary when the position of the ionization chamber changes. Also the angle that the anomalously reflected beam makes with the principal planes depends in a rather complicated manner upon the angle of incidence of the primary beam of rays on the crystal.

This anomalous reflection from the crystal is not a small phenomenon, its intensity being the third greatest of all the reflections in our experiments. We have also observed several very much weaker reflections from the crystal, which we have not yet thoroughly investigated. These weaker reflections have different critical voltages and therefore represent beams of different wave-lengths.

The reflection of a beam of x-rays characteristic of one of the chemical elements

in the crystal appears to be a difficult phenomenon to explain on the ordinary theory of reflection, without introducing new hypotheses.

**37. A study of secondary valence by x-rays.** GEORGE L. CLARK and WILLIAM DUANE, Harvard University.—By the new method of using x-rays in crystal analysis devised by the authors (Phys. Rev. 20, 84 and 85, 1922; Proc. Nat. Acad. Sci. 8, 90, 1922), crystals and powders of KI, $KI_3$, CsI, $CsI_3$ and $CsIBr_2$ have been investigated. As previously reported KI is simple cubic with a unit cube edge length of 3.532 A, and $KI_3$ monoclinic with $d = 4.68$ A. CsI is found to be cube-centered, with a distance between planes containing like atoms of 4.562 A. The first complete x-ray study of a rhombic crystal as represented by $CsI_3$ has been made in this investigation. The original method was extended by determining the complete spectrum by moving both crystal table and ionization chamber, for each of the sets of parallel planes at right angles (100, 010, and 001). Of great importance is the fact that the Cs and I characteristic effects are easily differentiated by the determination of wave-lengths by the critical voltage method. It is thus possible to determine separately the position of the atoms of each chemical element, even though they have neighboring atomic numbers. Four orders of Cs peaks showing marked absorption drops and $\alpha$- and $\beta$-peaks occur in every case before an I peak, which shows no sharp absorption drop on the short wave-length side. Numerous facts support the conclusion that in the unit parallelopiped containing 1 molecule the distances between planes bearing Cs atoms are 4.49 A (100), 6.50 A (010), and 7.04 A (001); and that the I planes are ¼ as far apart, so that one I atom is at the center of the parallelopiped and the other two so-called secondary valence atoms are equidistant on both sides along the body diagonal. $CsIBr_2$ has a similar structure with corresponding distances of 4.26, 5.91, and 6.90 A. An absolute series of parameters defining the position of the Br atoms is being experimentally determined.

**38. The crystal structure and densities of $Cu_2Se$ and ZnSe.** WHEELER P. DAVEY, General Electric Research Laboratory.—$Cu_2Se$ and ZnSe were made by the direct union of the elements. In the case of ZnSe the reaction took place with explosive violence. Both of these compounds show x-ray diffraction patterns of the diamond-cubic type. The $Cu_2Se$ crystals are composed of three interpenetrating face-centered cubic lattices, two of Cu and one of Se. These give a crystal structure similar to that of $CaF_2$. The side of each of the face-centered cubes is $5.751 \pm .007$ A. The ZnSe is composed of two interpenetrating face-centered cubes of side $5.651 \pm .007$ A, so that its structure is similar to that of ZnS. The densities of $Cu_2Se$ and ZnSe, as calculated from the x-ray data are, respectively, 7.154 and 5.283.

**39. The crystal structure of iron-nickel alloys.** L. W. MCKEEHAN, A. T. and T. and Western Electric Research Laboratories.—The variation of the face-centered cubic space lattice parameter with the addition of iron to nickel is followed at room temperature throughout the entire range from nickel to iron, and the variation of the body-centered cubic space lattice parameter with the addition of nickel to iron through the range from iron to thirty per cent of nickel. Speculations regarding the shapes and modes of connection of iron and nickel atoms are offered. The body-centered cubic space lattice of pure iron has $a = 2.872 \times 10^{-8}$ cm, corresponding to a density of 7.775 gm/cm³. The face-centered cubic space lattice of pure nickel has $a = 3.510 \times 10^{-8}$ cm, corresponding to a density of 8.953 gm/cm³.

**40. Thermionic phenomena due to alkali vapors. Part I. Experimental.** K. H. KINGDON and IRVING LANGMUIR, General Electric Research Laboratory.

*Electron Emission.*—If a tungsten filament be heated in a tube containing cæsium at 25° C, the cæsium vapor forms an adsorbed layer on the filament even at filament temperatures of 800° to 900° K, and at this temperature gives electron emissions as high as 0.3 amp. per cm². At higher filament temperatures the cæsium layer distills

off and the emission decreases. The temperature at which this occurs depends on the state of the surface of the filament. Similar effects have been observed with cæsium on nickel, molybdenum, and other filaments.

*Positive Ion Generation.*—A tungsten filament above 1100° K in cæsium vapor causes *every* atom that strikes its surface to leave as a positive ion. The saturation positive ion current is therefore given by $i_+ = ep(2\pi mkT)^{-1/2} = 0.367p/\sqrt{T}$ amp./cm², where $p$ is the pressure of cæsium vapor in bars and $T$ is the absolute temperature of the tube. From this formula values of $p$ were determined over a considerable temperature range. For example, at 24° C the vapor pressure of cæsium is 0.00166 bar. The saturation ion current is independent of filament temperature above the initial limit, and has been found to be the same for filaments of tungsten, carbon, and molybdenum in cæsium vapor. The ion current obeys the 3/2 power space-charge law.

**41. Thermionic phenomena due to alkali vapors. Part II. Theoretical.** IRVING LANGMUIR and K. H. KINGDON, General Electric Research Laboratory.

*Electron Emission.*—The emission from an adsorbed layer of cæsium on tungsten is analogous to that from thorium on tungsten. The emission from a cæsium surface as a function of temperature is expressed (within the probable error of the temperature measurements) by Dushman's equation $i_- = 60.2T^2e^{-(b_0/T)}$ amps./cm², where $b_0 = 15500$, corresponding to a value of 1.34 volts for the Richardson work-function $\phi$ for a cæsium surface.

*Positive Ion Generation.*—The electron affinity of a cæsium ion for the valence electron of the atom is 3.9 volts (ionization potential); whereas the electron affinity of a tungsten surface is 4.5 volts ($\phi$). Hence cæsium atoms leaving a tungsten surface are robbed of their valence electrons by the tungsten. Substances such as carbon ($\phi = 4.1$) and tantalum ($\phi = 4.3$) also generate positive ions from cæsium, whereas thorium ($\phi = 3.0$) does not. If there is much cæsium adsorbed on a tungsten surface $\phi$ becomes less than 3.9 volts and there is no positive ion generation ($\alpha$ state). At higher temperatures the filament becomes largely free from adsorbed cæsium ($\beta$ state) so that $\phi$ is greater than 3.9 volts and positive ions are generated. The transition from the $\alpha$ to the $\beta$ state is discontinuous. It is suggested that an electrode which generates positive ions under the conditions described above be called a *genode*.

**42. Theory of the temperature variation of the specific heat of hydrogen.** E. C. KEMBLE and J. H. VAN VLECK, Harvard University.—*Extension of quantum theory of specific heats of diatomic gases to cover vibrational as well as rotational motion.* A theory of the temperature variation in the specific heat of hydrogen based on the quantum hypothesis was described in a paper read before the Physical Society in 1917 (E. C. Kemble, Abstract, Phys. Rev. **11**, p. 156, 1918). The fundamental assumptions of that paper were those later used by Reiche (Ann. der Phys. **58**, p. 657, 1919) in developing the theory now generally accepted. But whereas Reiche has assumed a *rigid* dumb-bell model of the molecule, the paper in question was based on an elastic model and suffered from an error in connection with the calculation of the effect of the elasticity on the specific heat. The earlier theory has now been revised, taking into account both the vibrational motion of the molecule and the effect of the elasticity on the rotational specific heat. In order to simplify the calculations the law of force between the two atomic nuclei was assumed to have the form $F = a(r - r_0)/r^3$, where $r$ denotes the distance between the atomic centers and $r_0$ is its equilibrium value. By assuming suitable values for the constants $a$ and $r_0$ the model may be given any moment of inertia and any frequency of vibration. The energies of the stationary states can be cleanly evaluated and it is believed that the errors due to inaccuracy in the assumed law of force cannot be large below 1000° K. Thus an expression for the rotational and vibrational specific heat is derived, which

is found to agree well with the observations of Eucken, Scheel and Heuse, Escher, and Pier, over the entire range from 0° K to 2000° K. The empirical values of $r_0$ and $a$ yield $1.975 \times 10^{-41}$ gm cm² as the normal moment of inertia of the hydrogen molecule and $2.05\,\mu$ as the wave-length corresponding to its normal frequency of vibration.

*New empirical formulas for specific heats of hydrogen and water vapor derived from Pier's data.*—The empirical formula derived by Pier from his observations for the specific heat of hydrogen at high temperatures does not fit with the results of accurate measurements by others of the specific heat in the neighborhood of 20° C. A re-examination of his data yields the following new empirical formula not open to the above objection: $c_v = 4.87 + 0.539 \times 10^{-3}t + 0.146 \times 10^{-6}t^2$. Incidentally the following formula for the high temperature specific heat of water vapor follows from the same set of observations: $c_v = 6.03 + 4.2 \times 10^{-3}t - 4.07 \times 10^{-6}t^2 + 1.95 \times 10^{-9}t^3$. In these formulas $t$ denotes the temperature centigrade up to 2300°.

**43. Stages in the development of the iodine spectrum and related critical potentials.** F. L. Mohler and Paul D. Foote, Bureau of Standards.—In undissociated vapor below 10 volts apparently there are two stages in excitation of band spectrum, while above 10 volts both line and band spectra are obtained. Above 21 volts a second line spectrum appears. Dissociated vapor emits only pure line spectra. Electrical measurements gave critical radiation potentials at 10.5, 21, and 52 volts and probably others. Ionization was observed at 10.5, but no increase at 21 volts.

**44. Theory of the electric arc.** K. T. Compton, Princeton University.—A study of the simplest types of arc leads to the conclusion that thermionic emission from the cathode and sufficient gaseous ionization to neutralize the negative space charge around the cathode are the essential features. The way in which this emission and ionization are secured, as well as the conditions within the gas and at the anode, are of a secondary or accidental nature. The theory of the cathode drop is developed along two lines. (1) A consideration of the conditions of space charge and of electronic mean free path leads to the relation $J = 1.47(10)^{-7}(V_c^{3/2}M^{1/2}\lambda^2)$ amp. per cm², for the current density of positive ions in excess of the current density $j$ which is required to just neutralize the negative space charge. $V_c$ is the cathode fall of potential in volts, $M$ the molecular weight of the gas and $\lambda$ the electronic mean free path. $j$ is related to the current density $i$ of electrons by $i = 242\sqrt{M}\,j$. (2) A consideration of the energy relations at the cathode leads to an expression for the ratio of the current densities of positive ions and electrons of the form

$$\frac{n_2}{n_1} = \frac{\phi - fV_c + [(c + c' + R - H)/en_1]}{V_i + fV_c - \phi + (L/e)},$$

in which $\phi$ is the "work function" for the cathode; $c$, $c'$, and $R$ are the rates of energy loss by conduction, convection, and radiation from the cathode; $H$ is the rate of supply of heat by any external heating agency; $V_i$ is the ionizing potential of the surrounding gas; $L$ is the heat of reaction if gas molecules react with the cathode, and $f$ is a numerical factor depending on the geometry of the electrodes. Calculations of the fraction of total current carried by positive ions made by these two methods agree with each other within limits of accuracy imposed by the accuracy of existing experimental data. The positive ions carry only between 1 and 2 per cent of the total current in a carbon arc. The equations also show whether or not an arc can be maintained under given conditions without independent heating of the cathode.

**45. The electron theory and the Hall effect.** John A. Eldridge, University of Wisconsin.—It is generally supposed that the electron theory leads most naturally to a negative Hall coefficient for all conductors and the fact that many substances have

positive coefficients has been considered as showing that positive as well as negative carriers function in electrical conduction. Such a conclusion is not justified. The derivations such as that of Drude which have led to this result contain the unjustifiable assumption that the time of free flight of the conduction electrons is not altered by the applied electric field. When we take the free path rather than free time as unaltered (and assume the conductor to be isotropic) we find that the electron theory predicts no deflection whatever in a magnetic field. It is not surprising that a small positive or negative effect is found, since the simple assumptions of the theory can be only a very rough approximation to the truth. (See Phys. Rev. 21, 131, 1923.)

**46. Variation of capacity of photo-electric cells with illumination.** J. TYKOCINSKI-TYKOCINER,[3] University of Illinois.—A photo-electric cell represents a condenser in which the cathode and anode form the plates and the gas between them the dielectric. The distribution of electric lines of force in the dielectric varies with ionization. The capacity of the cell depends therefore on the illumination, which establishes a corresponding space charge in the gas, due to electrons expelled by light from the plate covered with photo-electrically sensitive material. Experimental verification of the variation of capacity of photo-electric cells with illumination was obtained by means of observing the plate current of a thermionic tube generating oscillations of constant frequency. In one of the experiments the oscillating circuit had two condensers in series. If to one of them a photo-electric cell was connected in parallel the plate current showed slight variations when the cell was illuminated by a varying source of light, proving that the illumination changes the capacity. By means of a telephone inserted in the plate circuit, loud sounds could be produced by a rotating sectored disc placed between the source of light and the photo-electric cell. Sounds were also obtained when only one of the electrodes of the cell was connected to the oscillating circuit.

**47. An equilibrium theory of electrical conduction.** A. T. WATERMAN, Yale University.—Accepting the simple electron theory expression for specific electrical conductivity, it is possible to explain the temperature variation of conductivity for good or poor conductors by a variation in concentration of free electrons, with a constant or nearly constant mean free path. Assuming that the electrons which may become free follow the ordinary laws of chemical equilibrium in their dissociation from the parent atoms, the following expression is derived for the specific resistance $\rho$: $(\nu+1)\ \log\ (\rho/c) = -\log\ \nu N + [(\nu+4)/2]\ \log\ T + (\phi_0 - \psi_0)/RT$, where $\nu$ is the valence of the atom; $N$ = number of atomic nuclei per unit volume; $T$ = absolute temperature; $R$ = gas constant per electron; $\phi_0 - \psi_0$ = mean energy required to render an electron "free" at 0° K; $C = 2\sqrt{3mR/A\epsilon^2\lambda}$, $A$ being due to a constant of integration. This formula, which is an approximation for values of the free electron concentration not too close to $N$, shows very fair agreement with experimental data on specific resistance for both good and poor conductors, and also accounts for metallic supraconductivity at low temperatures. For good conductors the requirement is that $\phi_0$ be very slightly less than $\psi_0$, for poor conductors that $\phi_0$ be considerably greater than $\psi_0$. In interpretation $\phi_0$ is identified with the photo-electric work function, while $\psi_0$ is the corresponding thermionic work function. According to the theory here proposed the ordinary expression for the thermionic saturation current becomes $\log i = [(4\nu+1)/2(\nu+1)]\log T - (\omega/RT) + \text{const.}$, where $\omega = (\phi_0 + \nu\psi_0)/(\nu+1)$, in the present notation. Therefore, for metals, where the conductivity expression indicates that $\phi_0$ and $\psi_0$ are nearly equal, the photo-electric $\phi_0$ and the thermionic $\omega$ as experimentally determined should be practically identical, which is found to be the case. On the other hand, for poor conductors, where $\phi_0$ is much greater than $\psi_0$, the experimental $\phi_0$ should be considerably greater than $\omega$, which again is in agreement with the facts.

[3] Introduced by Jacob Kunz.

On the basis of this theory it seems possible that light sensitivity in conduction may be due to a decrease in the value of $\phi_0$ by absorption of radiation of the proper frequency. For poor conductors, where $(\phi_0 - \psi_0)$ is a large positive difference, this would result in improved conductivity. For metals at ordinary temperatures the conductivity would not be sensibly affected, since $(\phi_0 - \psi_0)/RT$ is very small. According to this view, however, at low temperatures where this fraction becomes appreciable, metals should prove light-sensitive.

**48. The influence of variable electron mobilities on the formation of negative ions in air.** LEONARD B. LOEB,[4] University of Chicago.—In recent papers (Phys. Rev. **17**, 89, 1921; Phil. Mag. **43**, 229, 1922) the writer showed that the anomalous mobility curves for negative ions in air could be explained *qualitatively* by the use of a rough approximation to an equation proposed by J. J. Thomson (Phil. Mag., p. 321, 1915) to explain these curves. This theory assumes that an electron must make on the average $n$ impacts with gas molecules before it can attach to one to make an ion. At the time a closer agreement could not be obtained as the value of the electron mobility in air was not known. Recently the writer has succeeded in measuring the mobilities of the electrons in air for a limited range of pressures. The measurements are unfortunately not as accurate as could be desired because the range of measurements was limited by the formation of ions at the lower frequencies, by the inability to command frequencies higher than 180,000 cycles with the present apparatus, and by space-charge effects which disturbed the results at low field strengths. They showed, however, that the electron mobilities varied very little with voltage above 100 mm pressure, while at 40 mm they varied over a considerable range according to an equation of the form $K'p = 760\sqrt{a/(b+V)}$, where $V$ is the potential in volts, $p$ the pressure in mm, and $a$ and $b$ are constants which depend on the pressure. The negative ion mobility curves were then very carefully determined experimentally, under as nearly as possible the same conditions as those under which the electron mobilities were measured, particular care being taken to eliminate space-charge effects. The curves obtained were compared with the ion mobility curves computed from the rigorous equations of J. J. Thomson, as applied to the alternating current method of measurement, and were found to agree within the limits of certainty of the electron mobility curves. The values of $n$, the constant of attachment obtained from these measurements for air, lie between 2.20 and $1.80 \times 10^5$ for the range of pressures and frequencies used. For the same range of pressures in the original paper these values varied by a factor of 10, though the absolute average values are about the same. Thus, we may conclude that the attachment theory of J. J. Thomson is in all probability the correct explanation of the anomalous mobility curves for negative ions at low pressures.

**49. Ionization by charged corpuscles with velocities approaching that of light.** W. F. G. SWANN, University of Minnesota.—The paper extends the theory of ionization by rapidly moving corpuscles so as to include the reaction of the radiation emitted by the ejected electron. An electron which receives momentum from a rapidly moving corpuscle does so through an acceleration which approaches an enormous value as the velocity of the corpuscle approaches that of light. The reason for this lies in the great concentration which the field of a rapidly moving corpuscle suffers in its equatorial plane. An analysis of the situation shows that, for any assigned energy to be communicated to the electron, it is possible to calculate a velocity, less than that of light, and such that if the corpuscle has a velocity equal to or greater than this value it will fail to communicate the assigned energy to the electron. The result is of interest in enabling us to see how it is possible to admit, in our atmosphere, such corpuscles as are required by certain theories of the earth's charge, without encountering

[4] National Research Fellow.

unsurmountable difficulties in respect of the ionization which the corpuscles might be supposed, at first sight, to produce.

**50. The scattering of electrons by platinum and by magnesium.** C. DAVISSON and C. H. KUNZMAN, A. T. and T. and Western Electric Research Laboratories.—The angular distributions of electrons scattered by platinum and by magnesium have been examined for bombarding potentials up to 1,000 volts and 1,500 volts respectively. The experimental methods were those already described (Science, **54**, 524, 1921; Phys. Rev. **19**, 253 and 534, 1922). Up to 350 volts the scattering patterns for platinum are simple and similar in form to those required by theory for a nucleus surrounded by a single shell of electrons. Above 350 volts the distribution breaks up into a series of lobes which become more pronounced as the bombarding potential is increased. From 500 to 1,000 volts three lobes are found in the angular range $\Psi = 15°$ to $\Psi = 135°$ measured from the incident beam with another indicated at $\Psi = 0$. Such features were expected in the case of an atom as complex as that of platinum. The theory has not been sufficiently developed to make possible the analysis of these patterns. Magnesium was then deposited by vaporization onto the platinum target, and distribution patterns were again determined. The patterns are simple at all potentials to 1,500 volts, and are in accord qualitatively with the requirements of the theory. The results indicate a concentration of 7 or 8 electrons in the magnesium atom at a distance of about $1.5 \times 10^{-9}$ cm from its center.

**51. Positive rays in alkali metal vapor thermionic tubes.** HERBERT E. IVES, Western Electric Research Laboratory.—Thermionic tubes in which a quantity of alkali metal is present exhibit not only the normal electron current from the heated filament, but a positive current, which at low filament temperatures may be many times larger than the negative current. The electron current is in general reduced by the positive rays, but at higher filament temperatures the reduction of space charge by the positives causes a considerable increase of the current over a limited voltage range. By immersing the tube in liquid air the positive ray effects are almost eliminated, indicating that the alkali metal vapor is the source of the rays, which are probably produced by contact of metal atoms with the hot filament.

**52. The separation of the isotopes of mercury in a large steel apparatus.** WILLIAM D. HARKINS and S. L. MADORSKY, University of Chicago.—A small model consisting of one unit of a steel vacuum apparatus designed for the separation of mercury into isotopes has been constructed. Using this, a separation of 0.1 unit in the atomic weight of mercury has been obtained in 180 hours of operation combined with 25 hours operation of a still smaller apparatus. In the small model the mercury is heated electrically in a trough of 190 cc capacity, by an electric heating coil. The faster moving molecules escape more rapidly from the surface *D* than those moving more slowly. The molecules which evaporate strike the sloping ceiling of steel above *D* and collect into drops which slide down the slope and fall from the sharp "eaves," and finally collect in a capillary tube of more than barometric height at the bottom of the apparatus. The mercury collecting in this tube at any instant is 0.005 unit of atomic weight lighter in atomic weight than that in the trough, so the mercury in the trough becomes progressively heavier. The principle of the apparatus is the same as that of the small glass apparatus used by Mulliken and Harkins. The roof *B* is cooled by ice which is kept in the cylinder above it. If straight troughs are used to contain the mercury, and each trough is provided with its own slanting ceiling, many units may be put in a single vacuum chamber, so a very rapid separation could be made in this way. An apparatus of 10 kilos capacity has already been constructed. After the operation has begun, the operation of the apparatus is automatic except for the addition of mercury and the drawing off of samples.

**53. A high capacity apparatus for the partial separation of mercury into isotopes.** ROBERT S. MULLIKEN,[5] University of Chicago.—A high capacity apparatus has been built for the partial separation of mercury into isotopes by a combined evaporation and molecular diffusion method. The mercury is vaporized from a 500 cc flask in each of six large pyrex glass units. The jet of vapor passes up through a tube of filter paper about 1 meter long and 30 mm in diameter, which is fastened within an externally water-cooled glass tube, there being a space of 2 to 5 mm between the paper and glass tubes. The system is evacuated to an air pressure of 0.5 mm or less. Higher air pressures cause increased diffusion, but with reduced efficiency, by slowing down the vapor jet. At ordinary speeds of operation, the concentration of the vapor corresponds, it is estimated, to a pressure of about 6 mm. This is for an evaporation rate of about 500 cc per hour per unit, or about one ton in 20 hours for the six units together. About 80 cc per hour then diffuses in each unit, the remainder being condensed in an upper section of the unit, and falling back (through the upcoming vapor) into the flask for reëvaporation. The operation of the apparatus is carried on as a systematic fractionation. The six units are used independently but in cooperation. An experimental value of 0.0063 has been obtained by the writer for the separation coefficient of mercury in an apparatus similar to that here described, but in which the diffusion process could be studied separately from the evaporation. At the previously mentioned rate of operation, the efficiency of the evaporation process is about 1/5, and that of the diffusion about .77, the combined efficiency being about .92. The best compromise between speed and efficiency is found to be to run at such a speed that $E^{2.5}D$ is a maximum, where $D$ is the diffusion rate, and $E$ is expressed as a decimal. To determine this optimum speed, curves of speed *vs.* efficiency are obtained for each unit, using comparative density determinations as a measure of the change of atomic weight in a given operation.

In filling a unit at the beginning of a run, the lightest previously produced fraction of sufficient size is introduced into the apparatus. As the diffusion proceeds, the density of the residue in the flask steadily increases. In such an operation, the least dense and densest fractions produced become more widely separated at each repetition. A spread of 0.1 unit has now been obtained.

**54. Thermoelectric properties of sputtered films.** R. M. HOLMES, Cornell University.—Thermocouples consisting of a film and the metal from which the film was sputtered give the following e.m.f.'s when one junction is at 0° C and the other at 300° C: *gold*, 470 microvolts, the solid metal being positive at the cold junction; *platinum*, 2,720; and *palladium*, 7,700, with the films positive in the last two cases. With gold the e.m.f. is a linear function of hot junction temperature. With platinum and palladium there are breaks in the thermoelectric power lines due to heat treatment. If the films are baked at 500° C they become more like the solid metals. Thickness has no effect to within wide limits. In the case of platinum and palladium gas absorbed during the sputtering process is thought to make the film positive. Hydrogen absorbed during electrolysis makes bulk palladium positive to gas-free palladium, the thermoelectric power being 12 microvolts per degree at 0° C. This result is in agreement with the electron theory according to which the metal with the greater electron density is positive. The hydrogen will reduce the space available for electrons and also since the hydrogen atoms may themselves lose electrons the result will be an increase in electron density.

**55. Critical coupling and phase relations in V. T. power circuits.** N. H. WILLIAMS, University of Michigan.—An experimental method of determining the phase relation of high frequency currents has been devised, which makes the following investigation possible. The part of the work presented at this time deals with the phase relation of tube current to condenser current in the Hartley oscillator. In this circuit there

[5] Introduced by W. D. Harkins.

is a capacity coupling between the plate and the grid and also a magnetic coupling between the two coils that may be either positive or negative as related to the capacity coupling. When the coils are widely separated, the capacity coupling predominates and it makes little difference whether the magnetic coupling is positive or negative. With negative coupling when the distance between the coils is diminished, the frequency increases regularly and the phase difference decreases regularly until the condition is reached that makes the negative coupling predominate. At this critical coupling the frequency suddenly increases to about nine times its former value and the phase difference increases by about 80°. A mathematical analysis of the problem furnishes an explanation of the phenomena.

**56. Alkali vapor detector tubes with variable spacing of the electrodes.** CHAS. T. KNIPP and HUGH A. BROWN, University of Illinois.—At the recent Chicago meeting of the American Physical Society the authors gave the characteristics of various commercial three-electrode tubes, several of which had an electrode spacing of 3.5 mm from filament to plate and 1.5 mm from filament to grid, when they were primed with potassium-sodium alloy vapor. The striking characteristics of alkali vapor detector tubes were shown to be: low plate voltage for optimum audibility of response, non-critical adjustment of this voltage, and quite sensitive detector action at zero plate voltage.

The present paper deals with the effect of variable spacing of the electrodes. Special tubes were constructed of pyrex glass and of such form and dimension so that either the filament or the grid plate could be readily removed, each from its own end of the containing tube, and any desired adjustment made. When the distance between the plate and filament is reduced 30 to 50 per cent, the plate voltage for the best response is reduced from 10 volts to 5 or 6 volts, and the response at zero plate voltage is increased. It appears, however, that the efficiency of detection is not quite as good as for the standard spacings. Increasing the spacings of the electrodes, so that the distances from the grid and plate to the filament are 7 mm and 10 mm respectively, produces a very decided change in the detector characteristics. The response was found to be very weak at zero plate voltage, and to increase uniformly as the plate voltage increases until it reaches a maximum at from 40 to 50 volts. With this plate voltage the response increases rapidly as the filament temperature decreases until it reaches a maximum at a filament current approximately 50 per cent of normal. In this condition the tube is extremely sensitive on weak or medium received signal currents, producing 50 times greater response than the original tubes with the smaller spacing and containing no alkali vapor, and 10 times greater response than the smaller spacing tubes containing the alkali vapor.

**57. Scattering of particles by an Einstein center.** WILLIAM S. KIMBALL,[6] University of Michigan.—This paper considers the scattering of a stream of particles when Coulomb's inverse square law of force is replaced by Einstein's law corresponding to a fixed point center. The properties of the non-euclidean space time symmetrical about this center as considered here are given by Schwartzschild's solution of the field equations of gravitation: $ds^2 = dt^2(1 - 2l/r) - dr^2/(1 - 2l/r) - r^2 d\theta^2 - r^2 \times \sin^2\theta d\phi^2$. In the gravitation theory for an uncharged center, $l$, the constant of the center equals $\gamma m/c^2$, and the orbit is a close approximation to that due to Newton's law, $f = \gamma mM/r^2$. The corresponding substitute for Coulomb's law with dielectric constant unity replaces $\gamma mM/r^2$ by $NeE/r^2$, and hence makes $l = NeE/c^2M$. This choice of $l$ gives orbits approximating those due to Coulomb's law just as in the gravitation theory they approximate Newton's planetary orbits. The scattering is found to increase slightly with diminishing angle of deflection over and above the requirements of Rutherford's classical formula. It is actually in this way that Geiger and Marsden's data depart from classical requirements, but the experimental departure is large compared with the relativity departure.

[6] Introduced by H. M. Randall.

**58. The electrical conductivity of molybdenite.** A. T. WATERMAN, Yale University.—From experiments at constant e.m.f., at constant temperature, and at constant current, the following empirical formula for the current transmitted through small strips of molybdenite ($MoS_2$) in its ordinary state was found quite accurately to hold for a temperature range between 0° C and about 200° C: $i = KV^b e^{k/T}$, where $b = 1.6$ and $k = 3{,}000$, generally, and $K$ is a function of dimensions of strip, contact pressure, etc. The general phenomenon of breakdown, in the sense of a critical voltage maximum under application of increasing electrical power, is reviewed, and an expression derived for the temperature of the break, whence it is shown that in general the breakdown temperature should increase as $k$ decreases, until below a certain limiting value of $k$ no break should occur. Experiments with molybdenite show that either strong heating or high applied e.m.f., or both together in moderate degree bring about a large and nearly permanent decrease in resistance, approaching metallic conduction, but without change in appearance. Thus, under current heating in vacuum the resistance at room temperature may be transformed from several megohms to a few ohms. Under such treatment the constant $b$ decreases to unity, $k$ diminishes greatly and the breakdown temperature rises until the break disappears near the predicted value of $k$. The physical interpretation of $k$, as being proportional to the mean energy $\phi$ required to liberate an electron in the substance, results in a value $\phi = 0.26$ equivalent volt for the normal state, this value decreasing to less than half as metallic conduction is approached. It appears that dielectric polarization and liberation of electrons by application of an electric field may be involved in the normal conductivity. The most probable explanation of the semi-permanent change of state is a change in structure from an ordinarily stable form $\alpha$ of low conductivity to a form $\beta$ of good conductivity.

**59. The spectrum of neutral helium. II. Probability estimate and effects of wobbling of the nucleus.** LUDWIK SILBERSTEIN, Eastman Research Laboratory.—In order to show that the numerous coincidences obtained in the first paper on this subject (Astrophys. J., Sept. 1922) cannot be explained away as fortuitous, the probability of such a coincidence is calculated for a group of 44 lines, out of a total of 84 tabulated in that paper. This probability is shown to be as small as $10^{-19}$. In the second part of the paper the wobbling of the nucleus is explicitly taken into account. The corresponding supplementary terms of the energy of the atomic system are calculated and thence the value of the Rydberg "constant" is deduced. This is shown to harmonize with the compromise value used throughout the original table of lines.

**60. On the physical interpretation of results of line integrals of the earth's magnetic force.** LOUIS A. BAUER and W. J. PETERS, Department of Terrestrial Magnetism, Carnegie Institution.—At the Toronto meeting of the Society, the authors gave the results of line integrals of the earth's magnetic force taken around various complete circuits over ocean and land areas; the results were of such a magnitude and of such a character as not to be readily ascribable to observation errors (Phys. Rev. 19, 427, 1922). In accordance with usual theory, these results would be regarded as indicating the existence of electric currents passing perpendicularly through the area enclosed by the circuit. The current density thus indicated would be about 10,000 times that shown by atmospheric-electric observations. Some years ago another physical interpretation was suggested which has been reëxamined in the light of the more recent data and on the basis of a new analysis of the earth's magnetic field. It is found that the line-integral results reveal, in part at least, an effect similar to a deviation of the compass needle, which may be caused by forces set in operation during the earth's rotation; the compass needle is found to be deflected along a parallel of latitude, on the average, a few tenths of a degree towards the East in the Northern Hemisphere, and towards the West in the Southern Hemisphere.

**61. Certain optical properties of 60-inch parabolic mirrors.** E. B. STEPHENSON and NELS C. BENSON, Engineer Section, War Department.—Certain optical properties of large searchlight mirrors, especially those affected by the methods of manufacture and mounting in the searchlight, and the necessary apparatus and technique for rapid testing during the process of production were described and illustrated. The apparatus is sensitive to variations in focal length of approximately .02 cm and to variations in the thickness of the glass of approximately .001 cm. The line test consists in photographing the image of a large cross-ruled board as reflected in the mirror. The focus test consists in projecting a small narrow beam of parallel light onto selected points on the mirror and visually observing or photographically recording the image on a plate placed perpendicular to the optical axis at the principal focus of the mirror. The configuration of the resulting images in combination with the line test shows the optical properties of the mirror.

**62. The properties of very thin films of photo-electrically active material.** HERBERT E. IVES, Western Electric Research Laboratory.—Elster and Geitel discovered that the interiors of potassium photo-electric cells become everywhere coated with a thin layer of invisible but photo-electrically active material, which may be temporarily driven off by heating. Films of this sort have been observed by the writer, and measurements made of their photo-electric response distribution according to wave-length. These show that the photo-electric effect is of the "normal" type, increasing uniformly toward the violet, where the large mass of potassium in the same cell exhibits a strong "selective" effect.

**63. An extension of the fundamental infra-red absorption band of HCl.** W. F. COLBY, C. F. MEYER, and D. W. BRONK, University of Michigan.—The fundamental infra-red absorption band of HCl (center at about 3.46 $\mu$), originally investigated by Imes and later by Colby and Meyer, has been extended by the measurement of seven new lines on the long wave-length side. Using the previous notation, these lines are numbers −13 to −19 inclusive. The measurement of these additional lines was made possible by heating the absorbing gas to about 500° C and by using an echellette grating in the spectrometer so as to increase the available energy. A still more interesting result of this research has been the finding of a series of faint absorption lines which may correspond to a change in the vibrational quantum number "$n$" from 1 to 2. Five lines of this new series have been measured and have been designated as −XII, −XIII, −XIV, −XV and −XVI, since they fall between the lines −12 and −13, −13 and −14, −14 and −15, etc., of the principal series. It is not probable that any more lines of this series can be measured since on the long wave-length side the band runs into intense carbon dioxide absorption and on the short wave-length side the spacing of these lines is such that they would be hidden by the lines of the principal series.

**64. Crystal structure of manganese dioxide.** ANCEL ST. JOHN, Long Island City.—A modification of Hull's method of x-ray analysis has been used to determine the structure of polianite and pyrolusite. The defining slit is in contact with the specimen on the side toward the film and lies on the axis of the film. The lines are very sharp and fine. The scale requires no correction. Polianite is a body-centered tetragonal array of $MnO_2$ groups having an axial ratio 0.651, edges 4.44 A, and density 5.043. The oxygen atoms lie on a face-centered tetrahedral lattice and the manganese on a body-centered lattice, a manganese atom being at the center of alternate tetrahedra of oxygen atoms. The pattern of pyrolusite agrees line for line with polianite, hence any external form leading to its classification as orthorhombic is due to pseudomorphism.

**65. The separation of isotopes.** JAMES KENDALL, Columbia University.

*The ionic migration method.*—The principle of the moving boundary is here being utilized. An agar-agar gel containing chloride is inserted as a short middle section in a long horizontal tube, being preceded by a gel containing a faster anion (hydrox-

ide ion) and followed by a gel containing a slower anion (acetate ion). When a current is passed, the boundaries between the solutions remain perfectly sharp as the chloride moves slowly towards the anode. New tubes of hydroxide gel are inserted before it reaches its goal, and after it has travelled (say) 100 feet the chloride gel is sectioned and analyzed. If $Cl^{35}$ and $Cl^{37}$ ions possess different mobilities, the front sections should contain only the one isotope, the rear sections only the other. Runs are at present being made with chlorine and lithium. The products of the first chloride run are at present under analysis, and it is hoped to report results shortly. The importance of the application of this method to the *separation of the metals of the rare earths*, saving the laborious recrystallizations at present necessary, should be noted.

*The discharge potential method.*—Provided the familiar Nernst e.m.f. equation applies, the discharge potentials of the $Cl^{35}$ and $Cl^{37}$ ions in any solution should differ by about 0.03 volt. If now we can adjust our current so that it is just above the decomposition potential of one ion, and just below that of the other, and if we can withdraw the discharged products immediately, then a perfect separation should be possible. Probably the utmost that will be attainable in practice, however, will be an "electrolytic fractionation." The experimental details are now being developed and perfected before actual runs are made. Mercury, magnesium, and lithium are under investigation in this connection as well as chlorine.

*The freezing-point method.*—Although attempts to separate other isotopes by analogous methods have not succeeded in the past, it is possible that in an extreme case such as $Li^6$ and $Li^7$ an appreciable difference in the points of fusion of the pure isotopes will exist, and so permit a separation by fractional crystallization. This method is being tested out at the present time with lithium and potassium.

**66. A simple derivation of the Lorentz transformation.** H. M. DADOURIAN, Trinity College.—Let $S$ and $S'$ be two rectangular systems in uniform relative motion the $x$-axes of which are coincident and parallel to the direction of motion. Consider the coördinates of a point $P$ on the $x$-axis. If time is measured from the instant when the origins of the two systems coincide, then the $x$-coördinate of $P$, in the first system, is $x = vt + O'P$, where $v$ is the velocity of the second system relative to the first, $t$ is the time at which the position of $P$ is determined in the first system, and $O'P$ is the distance of $P$ from the origin of the second system as measured in the first system. Since space is considered to be homogeneous, $O'P = kx'$, where $x'$ is the $x$-coördinate of $P$ in the second system. Thus we have $x = vt + kx'$. Similarly, $x' = v't' + k'x$. When the point of view is changed from one to the other system the sense of the relative velocity is changed but not the magnitude, therefore, $v = -v$. On the other hand the distance between two points defined by two dots on a rigid bar is the same whether the bar is placed in the first system and measured from the second, or the conditions are reversed. This follows from the first postulate of the restricted theory of relativity. Therefore $k' = k$, and $x' = -vt' + kx$. Then we readily obtain: $x = (x' + vt')/k$; $t = [vt' + (1 - k^2)x']/vk$; $x' = (x - vt)/k$; $t' = [vt - (1 - k^2)x]/vk$. In order to determine the constant $k$ we apply the second postulate of relativity to the following special event. A beam of light leaves the common origin of the two systems at the instant $t = t' = 0$, and reaches the point $P$. Let $t_1$ and $t'_1$ denote the times indicated by the clocks of the two systems at the instant the ray reaches $P$. Then since the velocity of light is constant the position of $P$ is given by $x = ct_1$ in the first system, and by $x' = ct_1'$. These combined with preceding equations give: $x = x'(c + v)/ck$; $x' = x(c - v)/ck$. Hence, $k = \sqrt{1 - v^2/c^2}$. Introducing this value in equations for $x$, $x'$, $t$, and $t'$ we obtain the well-known transformations.